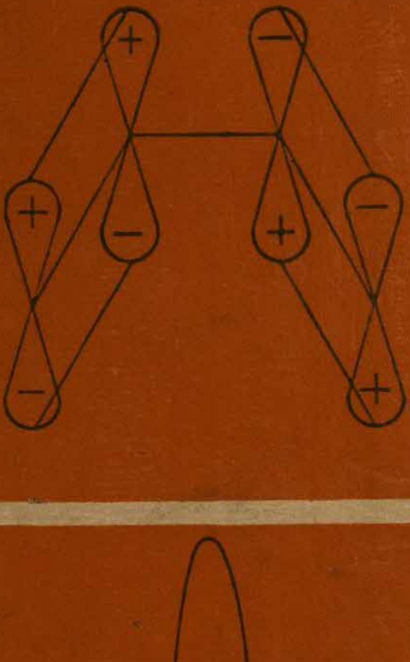
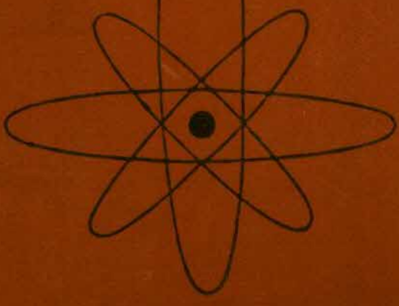
ELEMENTARY PHYSICAL CHEMISTRY

P. C. RAKSHIT





THE NEW BOOK STALL

ELEMENTARY PHYSICAL CHEMISTRY

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PREFACE

THIS BOOK has been written for the degree students. It covers the entire syllabus in Physical Chemistry for the undergraduate courses of all Universities in this country.

The present-day sophistication in the study of Chemistry as well as in other sciences needs introduction of a variety of new modern topics. In view of this, the chapters on wave theory in atomic structure, the chemical bonding, chemical kinetics, photochemistry, etc. have been made somewhat elaborate. Every attempt has been made to maintain the standard in an appropriate level so that the student may conceive and explain the physico-chemical phenomena from up-to-date theories.

Logical deduction based on precise reasoning appeals most to our thinking in exact science. That is why adequate stress has been given in precise derivation of equations with the mathematical apparatus available at the undergraduate level. These equations are indeed relations between physical quantities which should be understood and are not meant for memorisation. For this reason, the meanings of the mathematical formulae have always been explained in lucid language with simple illustrations so that the student may acquire the habit of realising the significance of the formulae. A number of worked-out examples follow each topic which would help the student to grasp the truth of the statements made in the previous section.

The subject of chemical thermodynamics has been developed from fundamental principles and its rigorous application in different types of equilibria—chemical, electrochemical and phase-equilibria—has been insisted upon.

Lucid explanation and discussion of the experimental behaviour of systems have been the general aim in the presentation of the topics. Exercises at the end of every chapter would prove useful.

The author will be very grateful to the teachers and students if they be kind enough to offer suggestions for the improvement of this book and to point out the inevitable errors which, inspite of every effort, creep in.

P. C. RAKSHIT

Calcutta
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PREFACE

This book has been written for Degree Course students. It covers the entire syllabus in Physical Chemistry for the degree examinations of all Universities in this country.

The present-day specialization in the field of Chemistry as well as in other sciences [illegible] of a variety of new and exciting topics. In view of these [illegible] changes, one more theory-oriented [illegible] the [illegible] chemical [illegible], photochemistry, etc. have been made somewhat elaborate. Every attempt has been made to maintain the treatment at an appropriate level so that the students may cultivate and [illegible] chemical phenomena from appropriate theories.

Logical deduction based on precise reasoning appeals most to one thinking [illegible]. That is why adequate stress has been given on proper derivation of equations with the mathematical apparatus available at the [illegible] level. These equations are exact relations between physical quantities which can be comprehended and are of [illegible]. For this reason [illegible] have always been explained in lucid language with simple illustrations so that the student may acquire the habit of grasping the significance of the [illegible]. [illegible] examples follow each topic which would [illegible] the truth of the statement made in the previous section.

The subject of classical thermodynamics has been developed from fundamental principles and its application to different types of equilibria—chemical, electrochemical and phase equilibria—has been emphasised upon.

Basic explanation and discussion of the [illegible] behaviour of systems have been [illegible] in the presentation of the topics. Exercises at the end of every chapter would prove useful.

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CHAPTER 1

THE PROPERTIES OF GASES

INTRODUCTION

The developing knowledge in any subject always leads to its division in different branches so that they can be conveniently studied separately. In chemistry, we deal with different kinds of matter, their changes and their interactions. When a large number of facts and the results of diverse investigations accummulated, it became necessary for chemistry as well to be divided into three broad sections: *Inorganic*, *Organic* and *Physical chemistry*. The first two are mostly descriptive. The organic branch deals with the detailed study of the element carbon and its innummerable compounds, whereas inorganic chemistry is concerned with all the remaining elements and their compounds. On the other hand, physical chemistry is the study of the general principles that govern all types of changes or reactions—organic or inorganic—whether occurring in nature or in the laboratories.

In the study of chemistry, as in all other sciences, we make **observations,** we perform *experiments* and collect data. Then we proceed to interpret those data in order to understand the behaviour of the matter under investigation. When a number of similar phenomena are observed and accurately studied, it becomes possible to make a statement which correlates the facts and which would predict the behaviour of other systems under similar conditions. Such a statement is called a **law.**

To explain the existence of such a law not only the experimental facts are sufficient, some speculations as to the probable cause of the phenomena or behaviour of the systems are also needed. A picture is mentally visualised which would explain the observed facts and the law deduced therefrom. Such a mental model with its predictions constitutes the **hypothesis** to explain the law. The truth in the suggestion of a hypothesis is then tested by fresh carefully planned experiments. If the predictions of the hypothesis are borne out from the results of fresh observations, the hypothesis developes into a **theory** for occurrences in the systems under investigation. The aim of the theory is to connect and coordinate apparently diverse phenomena and it also stimulates fresh experiments and enquiries.

To summarize, there are four stages in the progress of science: (*i*) observation and measurement (*ii*) inductive reasoning from the observed facts leading to a law (*iii*) suggestion of probable reasons to explain the facts, thus constituting a hypothesis and a theory (*iv*) testing the theories under diverse conditions.

An obviously satisfactory hypothesis (or theory) is not necessarily a permanent one. The discovery of new facts or more precise data may lead to discarding a so-far accepted theory. Science cannot be influenced by prejudice; it is based on truth. The rejection of a theory indeed helps in understanding nature more intimately and thus helps in the progress of science.

Even the students at school are now familiar with many of the elementary laws, hypothesis or theories of chemistry, e.g., the law of conservation of mass, the law of definite proportion and other stoichiometric laws and how these are derived from the Dalton's atomic theory, etc. etc., They are also familiar with Avogadro's hypotheis, the principle of equivalence etc.

The laws are very often expressed in mathematical language in some form of equations. The introduction of mathematical operations makes the ideas quantitative and accurate. The precision associated with the mathematical forms also leads to a clarity of thinking.

Physical Chemistry, expressed as laws in mathematical forms, thus gives a precise answer to 'why and how' a material transformation occurs. It predicts further the probability and impropability of a particular change in a given set of conditions. It even proceeds to find out the rate of progress of a chemical change.

The Mole Concept: The treatment or a discussion of any chemical phenomenon must always involve a system containing some amount of matter. There are different ways of measuring the amount of substance present in a system; the usual are mass, weight, volume etc. But the most convenient way of expressing the amount of substance for a chemist is in terms of '*moles*'. It can be defined in the following way:

Avogadro's number: We may remember the definition of Avogadro's number (N_0). It is the number of carbon atoms present in 12.000 grams of carbon (^{12}C). The value of Avogadro's number (N_0) is 6.02×10^{23}.

A mole of a substance is defined as the Avogadro number of molecules of the substance. Thus a 'mole' of CO_2 is the quantity carbon dioxide containing N_0 molecules of CO_2. The molecular mass of the CO_2 molecule is the sum of masses of the atoms of carbon and oxygen present, i.e. $2 \times 15.999 + 12.000 = 43.998$. From the definition of atomic masses and the mole, we know, the mass of a mole of $CO_2 = 43.998$ gm. This is indeed the gm-molecular weight in popular terminology. Hence the 'mole' of a substance would also represent its gm-molecular weight. To prevent any confusion, the Avogadro number atoms of an element, say bromine, would be a mole of bromine atoms. So the term 'mole' would stand for the Avogadro's number of a chemical unit or species. A mole of bromine atoms would be a *gm-atom* of bromine and correspond to 79.92 gm of bromine. In cases of compounds which exist in the dissociated or associated state, the mass of mole is taken as the gram-formula mass corresponding to the basic entity of the molecular formula. Thus, the mass of a mole of acetic acid (CH_3COOH) is taken as 60 gm though it is mostly present as dimers and that Na^+Cl^- is 58.45 gm though only ions occur in the crystal.

The convenience of using moles as measuring units of amounts lies in the fact that different substances always react in simple molecular proportions and, hence, in simple proportion of their gm-molecular weights, *i.e.* moles.

Before we proceed to understand and explain the different types of phenomena occurring in the material systems, it is necessary to be first conversant with the behaviour of matter in the different states of existence,—namely gaseous, liquid and solid states. We shall begin with the study of the properties of matter in the gaseous state.

1.1. The Gaseous State : Empirical Properties of Gases

The gases are characterised by the lack of definite volume or shape. In the gaseous state, the matter has the property of filling completely any available space to a uniform density. Low density and high compressibility are the pronounced characteristics of gases.

The behaviour of gases is often quite simple and many of their physical properties are identical for all gases, so that some simple rule would state the behaviour of all gases. To illustrate: the volume of a given mass of any gas is approximately halved when the pressure over the same is doubled (at const. temperature). This means that all gases have the same compressibility. Again, all gases are found to expand to the same extent when heated through same interval of temperature (at constant pressure). That is, all gases have the same coefficient of thermal expansion. On the other hand, the properties of solids and liquids differ appreciably from substance to substance; ether and water have quite different coefficients of compressibility.

The identity in behaviour of different gases is evident from the fact that all gases, irrespective of their chemical nature, size or weight of molecules, generally obey some simple and common relations, called the **Gas Laws.**

1.2. Boyle's Law

The volume of a given quantity of gas at a constant temperature is large at low pressure and small at high pressure. In 1662 Robert Boyle measured the variation of the volume of a gas with pressure and established the relation which is known as the Boyle's Law. It states:

At a constant temperature the volume (v) of a given mass of gas varies inversely as its pressure (P).

Hence $$v \propto \frac{1}{P} \qquad \ldots \text{(I.1)}$$

when mass of the gas (n moles) and temperature (T°K) remain constant.

or $$Pv = k_1 \text{ (constant)} \qquad \text{(I. 2)}$$

The relation between pressure and volume can then be represented by a rectangular hyperbola as shown in Fig. I.1. As the value of the constant in equation (I.2) will change with temperature, there will be a separate curve for each fixed temperature. These curves plotted at different fixed *temperatures* are called *isotherms*.

It is obvious from eqn (I.2) that if log v be plotted against log P a straight line will be produced with a negative slope. Further if Pv be plotted against P (at const. n and T), a straight line parallel to the P-axis will be obtained, since Pv is constant.

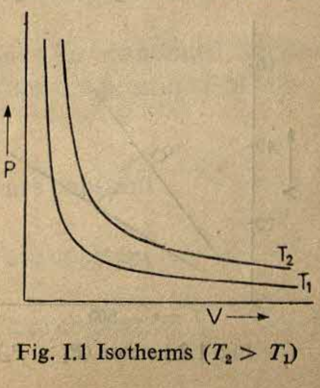

Fig. I.1 Isotherms ($T_2 > T_1$)

1.3. Gay-Lussac's or Charles's Law

The influence of variation of temperature on the volume of a gas was investigated by Charles (1787) and also by Gay Lussac (1802) independently. The quantitative relation derived from their experiments known as Gay-Lussac's Law or Charles's Law may be stated as,

At constant pressure, the volume of a given mass of gas expands by a constant fraction of its volume at 0°C *for* 1° *degree rise in temperature.*

If v_0 be the volume at 0°C and v at t°C of a given mass of gas at a constant pressure (P), then

$$v - v_0 = \alpha t v_0$$

or
$$v = v_0 (1 + \alpha t) \qquad \ldots (I.3)$$

where α is the coefficient of expansion.

Unlike that in solids or liquids, the value of α is approximately the same for all gases. The magnitude is determined by measuring the volumes of the gas at 0°C and at 100°C, so that, from equation (I.3),

$$\alpha = \frac{v_{100} - v_0}{100 v_0}$$

The precise determination of α led to an identical value for different gases.

$$\alpha = 0.0036609 = \frac{1}{273.16} \approx \frac{1}{273} \qquad \ldots (I.4)$$

We can express now the volumes of a given quantity of gas at t_1°C and t_2°C (at const. pressure) as

$$v_1 = v_0 \left(1 + \frac{t_1}{273}\right) \quad \text{and} \quad v_2 = v_0 \left(1 + \frac{t_2}{273}\right)$$

$$i.e. \quad \frac{v_1}{v_2} = \frac{273 + t_1}{273 + t_2} \qquad \ldots (I.5)$$

If the temperature of the gas be lowered to −273°C, then, from equation (I.3), the volume of the gas is reduced to zero. In other words, this temperature represents the limit of thermal contraction of the gas. This is indeed hypothetical because all gases would liquefy or solidify before reaching this limit.

A new scale of temperature with this limit as zero and having each degree equal to a centigrade degree has been devised and is called the *absolute scale or Kelvin scale of temperature*. The zero of the absolute scale is evidently −273°C; and 0°C will correspond to 273° Absolute, often expressed as 273°K. Any other temperature, say t°C will be $(273 + t)$°K.

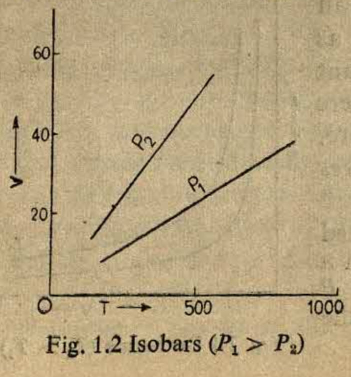

Fig. 1.2 Isobars ($P_1 > P_2$)

Rewriting equation (I.5), we have

$$\frac{v_1}{v_2} = \frac{273 + t_1}{273 + t_2} = \frac{T_1}{T_2}$$

where T_1 and T_2 are the temperatures in the absolute scale (°K).

The Charles's Law may be restated now :

The volume (v) *of a given mass of gas at constant pressure is directly proportional to its absolute temperature* (T).

Hence $v = k_2T$, (when n and P are constant). . . .(I.6)

On plotting volumes against absolute temperatures of the gas (at constant pressure), straight lines, called *isobars*, are obtained which on extrapolation shall cut the temperature axis at $T=0$°K where $V = 0$. (Fig. I.2).

The same line will be produced on plotting volume against temperature whether the latter is taken in absolute scale or in centigrade scale. The line will meet the temperature axis at 0°K (Fig. I.3).

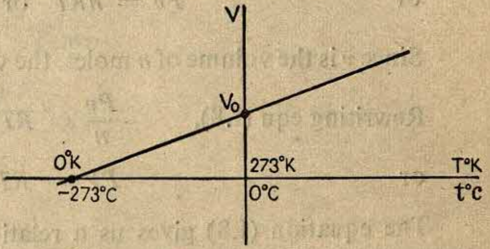

Fig. 1.3 Volume vs. Temperature

Again from equation. (I.6),

$$\log v = \log T + \log k_2;$$

hence the plot of $\log v$ vs. $\log T$ would be linear with a slope $\dfrac{\partial \log v}{\partial \log T} = 1$.

1.4. Avogadro's Law

In 1811, Avogadro discovered another law of nature for the gases. This is called Avogadro's Law, which states:

Measured at a common temperature and pressure, the volumes of same number of gram-moles of different gases would be the same. That is, at the same temperature and pressure, the volumes of n gm-moles of all gases would be the same.

Further it is common knowledge, that at any given temperature (T°K) and pressure (P), the volume (v) of a gas would be directly proportional to the quantity (n moles). Therefore, irrespective of the nature of the gas,

$v \propto n$, when P and T are constant *i e.* $v = k_3n$ . . . (I.7)

when $n = 1$, *i.e.* 1 mole of a gas is involved, $v = k_3$

That is, the volume of a mole of any gas is the same (at constant P and T).

1.5. The Equation of State

We can now make an attempt to correlate the gas laws just mentioned. Suppose a system containing n moles of a gas has a volume (v) under a pressure P at temperature T°K. Then from

(*i*) Boyle's Law: $v \propto \dfrac{1}{P}$, when n and T are constant

(*ii*) Charles's Law: $v \propto T$, when n and P are constant

(*iii*) Avogadro's Law: $v \propto n$, when P and T are constant

In other words, when all the parameters (n, P, T) vary independently, we have

$$v \propto \frac{nT}{P}$$

i.e. $v = R\,\dfrac{nT}{P}$, where R is a constant.

or $$Pv = nRT \quad \text{or} \quad \frac{Pv}{T} = nR \qquad \ldots \text{(I.8)}$$

Since v is the volume of n moles, the volume of 1 mole of the gas is $V = v/n$

Rewriting eqn (I.8), $$\frac{Pv}{n} = RT$$

or $$PV = RT \quad \text{(for 1 mole)} \qquad \ldots \text{(I.9)}$$

The equation (I.8) gives us a relation between pressure, volume and temperature (P, v, T) of a gas. Such a relation connecting (P, v, T) is called an *equation of state*. The equation can be employed to predict the behaviour of a gas under changes of temperature and pressure.

For 1 mole of a gas, $$\frac{PV}{T} = R \qquad \ldots \text{(I.9a)}$$

At any given temperature and pressure, the volume, (V) of a mole of any gas will be the same (Avogadro). Hence, R is a universal constant, called the *molar gas constant*.

The equation (I.8) is applicable to all gases and does not contain the characteristic of an individual gas. This relation is hence called the *ideal gas equation*. The gases strictly obeying this equation are named *ideal gases* or *perfect gases*.

The ideal gas equation is

$$Pv = nRT \qquad \ldots \text{(I.8)}$$

If g gm gas be present and M be its molecular wt. then the number of moles, $n = \dfrac{g}{M}$

So, $$Pv = \frac{g}{M}RT \qquad \ldots \text{(I.8a)}$$

Or $$PM = \frac{g}{v}RT = dRT \qquad \ldots \text{(I.10)}$$

since density of the gas, $d = \text{mass/volume} = g/v$

Alternatively, $$d = \frac{MP}{RT} \qquad \ldots \text{(I.10a)}$$

For a given gas (M, constant), the density of a gas is directly proportional to pressure at a constant temperature. This relation helps in calculating molecular weight of a gas from the measurement of density. Or, if the gas be known, the pressure can be computed from the density.

1.6. The Gas Constant R

$R = \frac{PV}{T}$, where V is the volume of one mole of gas. Dimensionally,

$$R = \text{Pressure} \times \text{Volume (per mole)} \times \frac{1}{\text{Temp.}}$$

$$= \frac{\text{Force}}{\text{area}} \times \frac{\text{Volume}}{\text{mole}} \times \frac{1}{\text{Temp}}$$

$$= \frac{\text{Force}}{(\text{length})^2} \times \frac{(\text{length})^3}{\text{mole}} \times \frac{1}{\text{Temp.}}$$

$$= \frac{\text{Force} \times \text{length}}{\text{mole} \times \text{Temp.}}$$

$$= \text{Work (i.e. energy) per mole per degree.}$$

Hence R has the units of energy per degree per mole.

The numerical values of R depend upon the units used for pressure, volume etc.

Values of R

At S.T.P., the volume of 1 mole of gas,
$V = 22414$ c.c. $= 22.414$ litres $= 22.414 \times 10^{-3}\, m^3$
The standard pressure, $P = 1$ atmosphere
$= 76 \times 13.6 \times 981$ dynes cm^{-2}
$= 1.013 \times 10^5\, Nm^{-2}$ (Newton/metre^2)
The normal temperature, 0°C $=$ 273°K.

(1) R in S.I. Units

$$R = \frac{PV}{T} = \frac{1.013 \times 10^5\,(N.m^{-2}) \times 22.414 \times 10^{-3}\,(m^3/\text{mol})}{273(°\text{K})}$$

$$= 8.3143 \text{ Joules } K^{-1}\,\text{mol}^{-1}$$

(2) R in litre-atmospheres

$$R = \frac{PV}{T} = \frac{1(\text{atm}) \times 22.414\ (\text{litres})}{273(°\text{K})} = 0.082 \text{ litre-atmospheres } K^{-1}\ \text{mole}^{-1}$$

(3) R in ergs

$$R = \frac{PV}{T} = \frac{76 \times 13.6 \times 981\ (\text{dynes/cm}^2) \times 22414\ (\text{cm}^3)}{273(°\text{K})}$$

$$= 8.314 \times 10^7 \text{ ergs } K^{-1}, \text{mol}^{-1}$$

Since 1 joule $= 10^7$ ergs

$$\therefore\ R = \frac{8.314 \times 10^7 \text{ ergs}}{10^7 \text{ ergs}} = 8.314 \text{ joules } K^{-1}\ \text{mol}^{-1}$$

(4) R in calories

Since 1 calorie = 4.184×10^7 ergs,

hence $$R = \frac{8.314 \times 10^7 \text{ ergs}}{4.184 \times 10^7 \text{ ergs}} = 1.987 \text{ calories K}^{-1}\text{ mol}^{-1}$$

$$\approx 2 \text{ calories. K}^{-1}\text{ mol}^{-1}$$

The values of *R per mole per* °K, may be compiled together:

$$\begin{aligned} R &= 8.3143 \text{ joules} \\ &= 0.08205 \text{ litre-atmospheres } (= 82.05 \text{ c.c.-atm.}) \\ &= 1.987 \text{ calories} \qquad \ldots (\text{I.11}) \end{aligned}$$

Boltzmann Constant: R represents energy per degree per mole. Hence RT would be energy per mole (at temp. T). This is obvious for RT equals PV, the latter being the product of pressure and volume would be work or energy.

N_0 is Avogadro's number, i.e. the number of molecules/mole. Hence, the energy per degree per molecule would be

$k = R/N_0 = (8.314 \times 10^7)/6.02 \times 10^{23} = 1.38 \times 10^{-16}$ ergs K^{-1} molecule^{-1} energy k is called the *Boltzmann constant*.

Extensive and Intensive Properties: The physical properties of systems such as pressure, volume, temperature, density, energy, viscosity, etc. have been classified into two groups: intensive and extensive. Intensive properties are those whose magnitudes are independent of the quantity of matter present in the system, such as temperature, pressure, density, viscosity, etc. A system may contain 1 kg or 100 kg of matter in a given state, the temperature would be the same. Extensive properties are those whose values are proportional to the mass of the system. Thus at a given temperature and pressure, the volume of ten moles of oxygen would be ten times the volume of one mole of oxygen.

It may be mentioned here that the energy (E) is always expressed as the product of two factors. It is obtained by multiplying an intensive property or factor by a capacity factor or extensive property. Thus,

mechanical work = $P.dV$, electrical energy = VdQ (volt-coulomb)
surface energy = $\gamma.dS$, etc.

1.7. Dalton's Law of Partial Pressures

If a vessel contains a mixture of two or more gases, then the individual pressures of the different gases will depend upon the relative proportions of the constituents. The individual pressures are usually expressed as the partial pressures of the constituents. The partial pressure of a constituent is defined as the pressure it would exert if it alone occupied the entire volume of the vessel at the same temperature. Dalton studied the relation between the partial pressures of the constituents and the total pressure of the mixture and stated his 'Law of Partial Pressures', as

The total pressure of a mixture of gases is equal to the sum of the partial pressures of the constituent gases (at the same temperature).

Thus, if a mixture of gases (temp. T) contains n_a, n_b, n_c, ... moles of different gases whose partial pressures are p_a, p_b, p_c, ... etc. respectively, the total pressure P of the mixture will be given by

$$P = p_a + p_b + p_c + \ldots.. \qquad (I.12)$$

Applying the equation of state which is independent of the nature of the gases, we have

$$P = \frac{n}{v} RT \qquad \ldots (I.13)$$

where v is the total volume of the system, and n = total number of moles $= n_a + n_b + n_c + \ldots..$

Again, the partial pressures are

$$p_a = \frac{n_a}{v} RT, \quad p_b = \frac{n_b}{v} RT, \quad p_c = \frac{n_c}{v} RT, \qquad \ldots (I.14)$$

Hence, $p_a + p_b + p_c + \ldots = \frac{RT}{v}\left(n_a + n_b + n_c + \ldots\right) = \frac{n}{v} RT$

Therefore, $\qquad P = p_a + p_b + p_c + \ldots$

Further, from equations (I.13 and I.14), we have

$$p_a = \frac{n_a}{n} P, \quad p_b = \frac{n_b}{n} P, \quad p_c = \frac{n_c}{n} P, \quad \text{etc.}$$

The partial pressure of a constituent can then be evaluated from the knowledge of the total pressure of the mixture and the relative proportion of the constituents.

1.8. Graham's Law of Diffusion

When a gas is enclosed in a vessel having porous walls, such as those of unglazed porcelein, earthenware, compressed graphite etc. the gas slowly escapes through the porous boundary. This is called *diffusion* of the gas.

On the other hand, if a gas escapes through a very fine artificially made orifice on the wall of the container, the process is called *effusion.*

Graham made an extensive study of both the diffusion and effusion of gases. He found that other conditions remaining the same, the rate of effusion or diffusion depends on the density of the gas; the heavier the gas the slower would be the rate. In 1832, Graham established a quantitative relation for such processes, called the *Graham's Law of Diffusion* (or *Effusion*). The law states:

At constant temperature and pressure, the rates of diffusion (or *effusion*) *of different gases through the same wall* (or *orifice*) *are inversely proportional to the square roots of their densities.*

The rate is the volume of gas escaping per unit time.

If r_1 and r_2 be the rates of diffusion (or effusion) for two gases having densities d_1 and d_2, then

$$r_1 = \frac{k}{\sqrt{d_1}} \quad \text{and} \quad r_2 = \frac{k}{\sqrt{d_2}}$$

or
$$\frac{r_1}{r_2} = \sqrt{\frac{d_2}{d_1}}\ ; \quad \text{i.e.,} \quad r\sqrt{d} \text{ is constant.}$$

In an effusiometer, same volume (v) of different gases are allowed to effuse out under the same pressure and temperature and the times required for escape are noted. Let t_1 and t_2 be the time needed by two gases to pass through the same orifice.

Then
$$\frac{r_1}{r_2} = \sqrt{\frac{d_2}{d_1}} \quad \text{(Graham's law)}$$

or
$$\frac{v/t_1}{v/t_2} = \sqrt{\frac{d_2}{d_1}} = \sqrt{\frac{D_2}{D_1}} = \sqrt{\frac{M_2/2}{M_1/2}} = \sqrt{\frac{M_2}{M_1}}$$

(D_1, D_2 are the vapour-densities)

or
$$\frac{t_2}{t_1} = \sqrt{\frac{M_2}{M_1}}$$

If the mol. wt. of one of the gases be known, the other can be computed by determining the times t_1 and t_2. Hence, Graham's law provides a method for the determination of molecular weight of a gas.

Another practical application of the Graham's law is in the partial separation of the components in a gas mixture. If the mixture is led through a tube made of porous walls, in a given time the lighter component will diffuse out more than the heavier one. By repeating the process with each separate fraction from diffusion, the concentration of one component can be considerably increased compared to that of the other. This is called *atmolysis*. Argon has been concentrated in nitrogen in this way. The isotopes of neon, chlorine, etc. have been partially separated by this method.

There is however some difference between effusion and diffusion processes. (1) In diffusion, the pores of the wall have almost the same dimensions as those of the molecules. As such, through each pore or passage, one gas molecule only can escape at a time.

On the other hand in effusion, even if the artificial orifice has a diameter of 2×10^{-3} cm, then its cross-section would be $\pi \times 10^{-6}$ sq. cm. The diameter of a molecule is of the order of 2×10^{-8} cm, so that its cross-section is $\pi \times 10^{-16}$ sq.cm. Hence, it is possible that at a time as many as 10^{10} gas molecules might escape through the hole.

(2) If a gas mixture diffuses through a porous wall, each component would escape independently governed by Graham's inverse sq. root density law. Thus, the two isotopes of neon when allowed to diffuse through a suitable wall, the diffusion co-efficient, $\epsilon = \sqrt{\frac{M_2}{M_1}} = \sqrt{\frac{22}{20}}$.

On the other hand, the rate of effusion of a mixture is inversely proportional to the square root of the mean density of the mixture.

1.9. Problems Worked Out

1. 7.0 gm carbon monoxide was contained in a 4-litre vessel at 47°C. Calculate the pressure.

From equation (I. 9),

$$P = \frac{g}{M}\cdot\frac{RT}{v} = \frac{7}{28}\times\frac{0.082\text{ (litre-atm) }\times(273+47)}{4\text{ (litres)}} = 1.64\text{ atm}$$

Or, using S.I. units,

$$v = 0.004\ m^3$$

$$P = \frac{7}{28}\times\frac{8.314\ J\times 320}{0.004\ (m^3)} = 166.28\times 10^3\ Nm^{-2}$$

$$= (166.28\times 10^3/1.01325\times 10^5) = 1.64\text{ atm.}$$

2. 12.8 gm of a gas occupies 10 litres at a pressure of 750 mm and 27°C. What is the mol. wt. of the gas?

From equation (I.9),

$$M = g\times\frac{RT}{Pv} = \frac{12.8\times 0.082\times 300}{(750/760)\times 10} = 31.91$$

Or, using S.I. units,

$$M = 12.8\times 10^{-3}\text{ (kg)}\times\frac{8.314\ (J)\times 300}{(750/760)\times(101325)Nm^{-2}\times 0.01\ (m^3)}$$

$$= 0.03191\text{ kg/mole}$$

$$\therefore \text{ The mol. wt.} = 31.91$$

3. What will be the density of H_2S at 27°C under a pressure of 2 atmospheres?

From equation (I.10a), using S.I. units,

$$d = \frac{MP}{RT} = \frac{0.034\text{(kg)}\times 2\times 101325(Nm^{-2})}{8.314(J)\times 300}$$

$$= 0.00277\text{ kg/litre} = 2.77\text{ g/litre}$$

Or, in litre-atmosphere units,

$$d = \frac{MP}{RT} = \frac{34\times 2}{0.082\times 300} = 2.77\text{ g/litre}$$

4. Determine the volume of 1.216 gm of SO_2 gas at 18°C and 755 mm pressure.

From equation (I.9)

$$v = \frac{g}{M}\cdot\frac{RT}{P} = \frac{1.216}{64}\times\frac{0.082\times 291}{(755/760)} = 0.4563\text{ litre}$$

5. On analysis a hydrocarbon was found to contain $C = 82.8\%$. At 75 mm pressure at 30°C temperature, the density of the gas was estimated as 0.2308 g/litre. Find out its formula.

From equation (I.10a), the mol. wt. of the gas,

$$M = \frac{dRT}{P} = \frac{0.2308\times 0.082\times 303\times 760}{75}$$

$$= 57.89\text{ gm/mole}$$

$$\therefore \text{ mol. wt.} = 57.89$$

But proportion of C : H 82.8 : 17.2 .
that atomic proportion $= (82.8/12) : (17.2/1)$
$\approx 2 : 5$

Hence the empirical formula is, C_2H_5
∴ molecular formula $(C_2H_5)_x$, mol. wt. $= 29x$. The estimated value 57.89 suggests $x = 2$.
Hence its mol. wt. $= 29 \times 2 = 58$
The molecular formula is C_4H_{10}

6. A gas from a litre flask is evacuated until the pressure became as low as 10^{-7} cm of Hg at 28°C. How many molecules of the gas are still left in the flask?

Suppose x molecules still exist in the flask.
x molecules $= (x/N_0)$ moles, N_0 = Avogadro number.

From equation (I.9), $PV = nRT = \frac{x}{N_0}RT$

$$\text{Or} \quad x = \frac{N_0PV}{RT} = \frac{(6.02\times10^{23})\left(\frac{10^{-7}}{76}\right)\times 1}{0.082\times301}$$

$$= \frac{6.02\times10^{16}}{0.082\times76\times301} = 3.2 \times 10^{13} \text{ molecules}$$

7. Two litres of methane at 600 mm pressure and one litre of ethylene at 500 mm pressure were introduced at a const. temp. into a 4-litre flask. What would be the total pressure?

Let p_1 and p_2 denote the partial pressures of CH_4 and C_2H_4. Then for methane,

$$p_1 \times 4000 = 2000 \times 600$$
$$\text{or } p_1 = 300 \text{ mm}$$

For ethylene, $p_2 \times 4000 = 1000 \times 500$, or $p_2 = 125$ mm

∴ Total pressure, $P = p_1 + p_2 = 300 + 125 = 425$ mm

8. A monkey inhaled air containing 20% oxygen and the exhaled gas contained 16% oxygen, both estimated on a dry basis. In a metabolic study, the air exhaled out in 5 minutes, collected over water, was 40 litres at 20°C and 757 mm. At 20°C, aqueous tension is 17 mm. Calculate the rate of oxygen consumption (at S.T.P.) per minute .

If p_1 be the partial pressure of O_2 in the exhaled air, then

$$p_1 + p_{H_2O} = p = 757$$
$$\text{or} \quad p_1 = 757 - p_{H_2O} = 757 - 17 = 740 \text{ mm}$$

The volume of exhaled air, $v = 40 \times \frac{273}{293} \times \frac{740}{760} = 36.2$ litres

$$\therefore \text{ Rate of } O_2 \text{ consumed} = \frac{\text{Vol. of } O_2 \text{ used up}}{\text{time}} = \frac{36.2\left(\frac{20}{100} - \frac{16}{100}\right)}{5 \text{ (min)}}$$

$$= 0.2896 \text{ litres/min}$$

$$= 289.6 \text{ c.c./min}$$

9. Ladenburg found that a sample of ozonised oxygen containing 86.16% of ozone by weight required 430 seconds to diffuse under conditions where pure oxygen required 367.5 seconds. Determine the vapour density of ozone.

Let v be the volume diffusing out in each case. Let d_m, d_o and d be the densities of the mixture, pure oxygen and ozone respectively.

$$\frac{v/430}{v/367.5} = \sqrt{\frac{d_o}{d_m}} = \sqrt{\frac{16}{d_m}}$$

or
$$d_m = \left(\frac{430}{367.5}\right)^2 \times 16 \approx 21.91$$

Again for 100 gm, the volume, $\frac{100}{d_m} = \frac{86.16}{d} + \frac{13.84}{d_o}$

or
$$\frac{100}{21.91} = \frac{86.16}{d} + \frac{13.84}{16}$$

whence
$$d = 23.3$$

10. A mixture of oxygen and helium containing 10 mole percent of the latter diffused out through a porous wall of the container. What would be the proportion of the two gases when they come out initially?

molar proportion; $O_2 : He = 90 : 10$

∴ Ratio of their partial pressures, $P_{O_2} : P_{He} = 9 : 1$

Hence, the ratio of their rates of diffusion,

$$\frac{R_{O_2}}{R_{He}} = \frac{\sqrt{P_{O_2}/d_{O_2}}}{\sqrt{P_{He}/d_{He}}} = \sqrt{\frac{P_{O_2} \times d_{He}}{P_{He} \times d_{O_2}}} = \sqrt{9 \times \frac{4}{32}} = 3 : 2.82$$

or $V_{O_2} : V_{He} = 3 : 2.82$ (by volume)

11. A half-litre bomb at 27°C is filled with C_2H_4 at 1 atm. and oxygen at 5 atm. and the mixture is exploded. Calculate the final pressure if final temperature is 127°C.

For C_2H_4 : $P_{C_2H_4} \times 0.5 = nRT$, or $n = \frac{1 \times 0.5}{RT} = \frac{0.5}{RT}$

For O_2 : $P_{O_2} \times 0.5 = n'RT$, or $n' = \frac{5 \times 0.5}{RT} = \frac{2.5}{RT}$

Since $C_2H_4 + 3O_2 = 2CO_2 + 2H_2O$

$\frac{0.5}{RT}$ moles of C_2H_4 used up $\frac{3 \times 0.5}{RT}$ or $\frac{1.5}{RT}$ moles of O_2

Hence, residual oxygen $= \frac{1.0}{RT}$ moles, CO_2 (produced) $= \frac{2 \times 0.5}{RT}$

$= \frac{1.0}{RT}$ moles

At 127°C, the water produced would be gaseous and its amount is equal to that of CO_2. Hence, water vapour $= \frac{1.0}{RT}$ moles. Total $= \frac{3.0}{RT}$ moles.

∴ The final pressure, (at 400°K) $P = \frac{nRT}{v} = \frac{3}{R \times 300} \times \frac{R \times 400}{0.5}$

$= 8$ atm.

EXERCISES

Equation of State

1. Compute the weight of a litre of CO_2 at S.T.P. [Ans. 1.964 g]

2. One gm of He is confined in a 2-litre flask under a pressure of 2.05 atm. What is its temperature? [Ans. −73°C]

3. Calculate the volume occupied by 2.432 g of SO_2. The pressure is 755 mm and temp. 18°C. [Ans. 0.913 l]

4. What volume will 7.50 gm argon occupy at 90°C and 735 mm? [Ans. 576.8 cc]

5. Find the total pressure exerted by 1.60 gm methane and 2.2 gm CO_2 contained in a 4 litre flask at 27°C. [Ans. 700 mm]

6. Calculate the mol. wt. of a gas whose density at 40°C and 392.5 mm is 0.643 gm per litre. [Ans. 32]

7. At 100°C and 0.5 atm, the density of a gas is 0.72 gm/litre. What is its mol. wt? [Ans. 44.04]

8. What weight of CO_2 at 750 mm and 27°C could be contained in a vessel that holds 8 gm O_2 at the same temp. and pressure? [Ans. 11.0 gm.]

9. Estimate the density of H_2S gas at 27°C and 4.00 atm. [Ans. 5.54 g/l]

10. At 0°C the density of a gaseous oxide of a non-metal at 2 atm was found to be same as that of O_2 at 5 atm. Find the mol. wt. of the gas. [Ans. 80]

11. At $T = 291°K$ and $P = 765$ mm, 0.645 litre of a gas weighs 1.355 gm. What is its mol. wt? [Ans. 49.8]

12. Find the number of molecules of a gas present per cc in a vessel evacuated to a pressure of 10^{-6} mm at 27°C [Ans. 3.2×10^{10}]

13. A 500 c.c. vacuum tube was sealed off when the pressure was 1.2×10^{-6} cm at 27°C. How many molecules are still left inside? [Ans. 1.9×10^{14}]

14. In an evacuated vessel 4 gm of a gas A is introduced when the pressure, was found to be 720 mm. The experiment was repeated with gas B, when the pressure was found to be 360 mm. The temperature was kept constant. If the first gas be methane can you suggest the name of gas B.

Partial pressures

15. What will be the pressure if ½ litre H_2 at 500 mm and 1 litre O_2 at 400 mm be introduced into a litre vessel at 27°C? [Ans. 650 mm]

16. 40 gm H_2 and 140 gm N_2 are kept at a pressure of 20 atm. What are their partial pressures? [Ans. 16 atm, 4 atm]

17. A gas mixture contains 20% by weight of H_2 and 80% by weight of O_2; the total pressure is 1 atm. Calculate the partial pressures. [Ans. $P_{H_2} = 608$ mm]

18. The composition of air is N_2 79 mole percent, O_2 20 mole percent, and argon 1 mole %. Calculate the partial pressures exerted by these components at 1 atm and 27°C. [Ans. $P_{N_2} = 0.79$ atm]

19. The electrolytic gas produced from electrolysis of 6 gm water was collected in 10 litre vessel at 27°C. What are the partial pressures of H_2 and O_2? [Ans. $P_{H_2} = 0.82$ atm., $P_{O_2} = 0.41$ atm]

Graham's Law of diffusion

20. What will be relative rates of effusion of the following pairs of gases through a fine pinhole: (*a*) nitrogen and carbon monoxide, (*b*) hydrogen and carbon dioxide and (*c*) methane and oxygen [Ans. (*a*) 1 : 1 (*b*) 4.7 : 1 (*c*) 1.4 : 1]

21. At what pressure will oxygen at 0°C diffuse at the same rate through the same wall as methane at 1 atm and 0°C? [Ans. 2 atm]

22. A gas required 50 sec to escape through a fine orifice in an effusiometer. Under identical conditions, nitrogen required 35 seconds. What is the mol. wt. of the gas. [Ans. M = 57.2]

23. A sample of water vapour was prepared containing 50 mole % of heavy water. If this sample is allowed to diffuse out, what would be relative proportion in the initial vapour diffusing out. [Ans. 1.054 : 1]

Miscellaneous

24. (i) Express R in (*a*) c.c.-atm degree^{-1} (*b*) volt-coulombs degree^{-1}
   (ii) Find out the mol. wt. of a gas which is three and-a-half times as dense as oxygen at same temp. and pressure
   (iii) At 0°C, the vapour pressure of mercury is 1.2×10^{-3} mm Hg. Estimate the concentration of mercury in moles per litre in the Torricelli's space in a barometer.
   [Ans. (*ii*) 112, (*iii*) 7.05×10^{-8}]

25. The coefficients of expansion and of compressibility are given by $\alpha = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_P$ and $\beta = -\frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_T$. What would be these values for ideal gases? $\left[\text{Ans. } \frac{1}{T}, -\frac{1}{P}\right]$

26. At a constant pressure of 0.41 atm, the volume (V) of a system containing argon was measured at different temperatures (T). the plot of log V against log T made an intercept of -1.301 units on the log V-axis. How much argon was present in the system? [Ans. 10 gm]

27. A one-litre flask at 27°C contained equimolar mixture of O_2 and SO_2 gases. The total mass of the gas mixture was 3.60 gm. Calculate the total pressure. [Ans. 1.845 atm]

28. Equal masses of He and O_2 were taken in two flasks of the same capacity at a constant temperature. (*i*) which flask contains more molecules and how many times as many? (*ii*) In which flask the pressure is higher and how many times higher? [Ans. 8 : 1, 8 : 1]

29. An asthmatic patient was provided with oxygen-rich air with 50%O_2; his exhaled gas contained 44% O_2, both measured on dry basis. The air exhaled in 10 min collected over water was found to be 60 litres at 752 mm and 30°C (f = 32 mm). Calculate his rate of consumption of O_2 measured at N.T.P. [Ans. 306 c.c./min]

30. From the two opposite ends of a 50 cm narrow tube, two gases Cl_2 and H_2S are introduced. At what point of the tube would sulphur be first deposited?
[Ans. 29.55 cm from the H_2S end]

31. Two flasks of equal capacity contained two different ideal gases. The pressures of both were equal but the temperature (°K) of the 1st was three times that of the 2nd. Calculate the ratio of the number of molecules in the two flasks. [Ans. 1 :3]

32. 1.4 gm carbon monoxide was introduced into a 4-litre flask already containing some oxygen. The flask was heated to a temperature of 127°C, when the pressure was 191.5 mm. Calculate the quantity of oxygen in the flask. [Ans. 0.32 gm]

33. If a gas (M = 30) contained in a vessel of fixed volume of 1000 c.c. at 27°C exerts a pressure of 1 atm on its wall of 100 cm^2, what will be the new pressure if (*i*) the temp. is raised to 54°C, (*ii*) the gas is replaced by a equal number of molecules of mol. wt. 45, (*iii*) the gas is replaced by an equal weight of another gas (M = 60). (*iv*) the walls had an area of 50 cm^2?

[Ans. (*i*) 1.09 atm (*ii*) 1 atm (*iii*) 0.5 atm (*iv*) 1 atm]

CHAPTER 2

THE KINETIC THEORY OF GASES

All gases irrespective of their nature obey the empirical laws mentioned in the previous chapter. The identity in behaviour of different gases suggests that there is some inherent common or similar character in their physical nature. Attempts to interpret quantitatively the observed properties of gases started more than two centuries ago. It was Bernoulli (1738) who first described mechanically the properties of gases. That gases were composed of minute particles was accepted quite early. Their property of spontaneously filling entire available space as well as their diffusion convinced the existence of diverse motion of those particles. These basic ideas formed the root of the theory to explain the behaviour of gases. This is now called the *Kinetic Theory of Gases.* The present state of the theory developed as a result of the thoughts and contributions of not one but a host of great minds spread over centuries. In the last century, especially through the efforts of Joule, Kronig, Clausius, Boltzmann, Maxwell, the theory succeeded to attain a rigid mathematical form.

2.1 The Kinetic Theory

The kinetic theory, like other theories, is based on some simple postulates or assumptions. These postulates may be summarised as follows:

(1) Gases are composed of minute discrete particles, now called molecules. In any one gas, all the particles are of the same size and mass.

(2) The molecules of a gas are in a state of ceaseless chaotic motion in all possible directions with very high velocities. They incessantly collide with each other and with the walls of the container. Between two successive collisions, a molecule moves in a straight line.

(3) The molecules exert no appreciable attraction on each other and are supposed to be perfectly elastic. Hence no energy is lost from their collisions.

(4) The dimensions of the molecules are negligible. The actual volume occupied by the molecules is negligible compared to the volume of the gas. The molecules are regarded as point masses.

(5) The average force per unit-area that the molecules exert in their impacts on the walls is the *pressure.* The larger the number of impacts, the greater will be the pressure.

(6) The *absolute temperature* of a gas is a measure of the average kinetic energy of the molecules of the gas. The average kinetic energy is proportional to the absolute temperature of the gas.

The kinetic energy here presumes the translational kinetic energy only of the molecules due to their linear motions.

These assumptions constitute the kinetic-molecular concept for gases. If the temperature is raised, the molecules move more vigorously and there would be a larger number of impacts on the walls (at a constant volume). That is why we find an increase of pressure with rise in temperature at a const. volume. On the other hand, if volume is decreased at a const. temperature, the molecules would strike the wall more frequently leading to higher pressure, a fact experimentally confirmed.

2.2. Velocity of gas molecules

At any instant, the randomly moving particles in a gas possess different velocities, some high and others low velocities. Due to incessant collisions, the velocity of any given molecule must always be constantly changing both in direction and in magnitude. To visualise the state of their motion, some sort of mean value for the velocities of the molecules has to be conceived.

Suppose there are N molecules present in a given quantity of a gas. Out of these N molecules, let us say, there are

n_1 molecules with velocity c_1 and kinetic energy ϵ_1,
n_2 molecules with velocity c_2 and kinetic energy ϵ_2,
n_3 molecules with velocity c_3 and kinetic energy ϵ_3, etc.

Then $N = n_1 + n_2 + n_3 + \dots$

The total translational kinetic energy (E) is given by

$$E = n_1\epsilon_1 + n_2\epsilon_2 + n_3\epsilon_3 + \dots$$

(*i*) The arithmetic mean of the velocities of the molecules, called *average velocity*, c_a, is given by

$$c_a = \frac{n_1c_1 + n_2c_2 + n_3c_3 + \dots}{N} = \frac{\Sigma n_ic_i}{N} \qquad \dots (II.1)$$

(*ii*) But a different kind of averaging is also possible and it is often used. The sum of the squares of the velocities would be

$$n_1c_1^2 + n_2c_2^2 + n_3c_3^2 + \dots = N\overline{c^2} \qquad \dots (II.2)$$

where $\overline{c^2}$ is the mean of the squares of all the velocities. $\overline{c^2}$ is called *mean square velocity.*

$$\overline{c^2} = \frac{n_1c^2 + n_2c_2^2 + n_3c_3^2 + \dots}{N}$$

Taking the root,

$$c = \sqrt{\frac{n_1c_1^2 + n_2c_2^2 + n_3c_3^2 + \dots}{N}} = \left(\frac{\Sigma n_ic_i^2}{N}\right)^{\frac{1}{2}} \qquad \dots (II.3)$$

c is called the *root mean square velocity* (r.m.s. velocity). It is evident that the two mean velocities are not the same. For example, suppose there are five molecules having speeds 3, 4, 5, 6 and 7 metres/sec.

Then $c_a^2 = \left(\frac{3+4+5+6+7}{5}\right)^2 = 25\ \text{m}^2/\text{sec}^2.\ ;\quad c_a = 5\ \text{m/sec}$

and $c^2 = \left(\frac{3^2+4^2+5^2+6^2+7^2}{5}\right) = 27\ \text{m}^2/\text{sec}^2.\ ;\ c = 5.196\ \text{m/sec}$

The relation between the two ; $c \approx 1.805\, c_a$; or $c_a = 0.9213\, c$

In some cases, the use of mean square velocities are quite important. For example, the total energy of the molecules (when m is the mass of a molecule),

$$\begin{aligned} E &= n_1\epsilon_1 + n_2\epsilon_2 + n_3\epsilon_3 + \dots \\ &= n_1.\tfrac{1}{2}mc_1^2 + n_2.\tfrac{1}{2}mc_2^2 + n_3.\tfrac{1}{2}mc_3^2 + \dots \\ &= \tfrac{1}{2}m\,(n_1c_1^2 + n_2c_2^2 + n_3c_3^2 + \dots) \\ &= \tfrac{1}{2}\,mN\overline{c^2} \text{ (from equation II.2)} \end{aligned}$$

Since energy-terms involve square of velocities, so in averaging it is not only convenient and reasonable but also more accurate to apply mean square velocity in computing average energy.

2.3. The pressure of a gas

The postulates of the kinetic theory enable us to calculate the pressure of a gas in terms of molecular quantities.

Let us consider a volume of gas contained in a cubical box of side l. Let the number of molecules present in it be N, the mass of each molecule being m.

The molecules are moving constantly with different velocities in different directions bombarding on the walls of the cube. Consider any one molecule and suppose its velocity is c_1 at a given instant. The velocity c_1 may be resolved into three rectangular components x_1, y_1 and z_1 along the axes parallel to the three edges of the cubical box. Then

$$c_1^2 = x_1^2 + y_1^2 + z_1^2$$

Now consider the motion of this molecule along x-axis perpendicular to the walls G and H of the vessel (Fig. II.1).

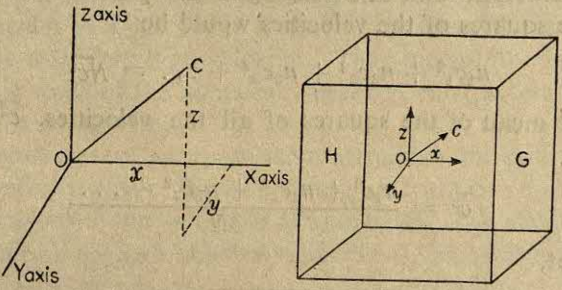

Fig. II.1

The collisions being perfectly elastic, the molecule after striking the wall G with velocity x_1 returns with exactly the same velocity but in opposite direction. The momentum of the molecule just when it strikes is mx_1 and when it rebounds, magnitude of the momentum is $-mx_1$. The mugnitude of change of momentum due to a collision is therefore $mx_1 - (-mx_1) = 2mx_1$.

It is obvious that after its collision with the wall G, it will travel a distance l to make an impact on the opposite wall H and then return to G again. So, after moving a distance l every time, it will make an impact on a wall. The total number of collisions the molecule makes on the two opposite walls in unit time would be $\frac{x_1}{l}$.

Therefore, the total momentum-change due to collisions on walls G and H by this molecule per second $= \frac{x_1}{l} \times 2mx_1 = \frac{2mx_1^2}{l}$

If we now consider the directions along Y-axis and Z-axis, the momentum change due to the collisions of this molecule on the corresponding pairs of walls would be $\frac{2my_1^2}{l}$ and $\frac{2mz_1^2}{l}$. per second.

Hence, the net momentum-change for the collisions of this molecule on all the six walls per second is $\frac{2m(x_1^2 + y_1^2 + z_1^2)}{l} = \frac{2mc_1^2}{l}$

Let there be $n_1, n_2, n_3, \ldots$ molecules having different velocities $c_1, c_2, c_3 \ldots$ etc. The change of momentum per second from collisions of all the molecules on all the walls would be

$$\frac{2mn_1c_1^2}{l} + \frac{2mn_2c_2^2}{l} + \frac{2mn_3c_3^2}{l} + \ldots$$

$$= \frac{2m}{l}(n_1c_1^2 + n_2c_2^2 + n_3c_3^2 + \ldots) = \frac{2mN\overline{c^2}}{l}$$

where $\overline{c^2}$ is the mean square velocity.

This change of momentum per unit time is the force F exerted by the molecules (Newton's Law) on all the walls,

$$i.e., \qquad F = \frac{2mN\overline{c^2}}{l}$$

The pressure of the gas P is the force per unit area. There are six walls each of area l^2. Hence the total force on all the walls,

$$F = 6l^2 \times P$$

That is, $\quad P = \frac{F}{6l^2} = \frac{2mN\overline{c^2}}{6l^3} = \frac{1}{3}\frac{mN\overline{c^2}}{v},$

since $\quad l^3 = v$, the volume of the cube.

Hence $\quad Pv = \frac{1}{3}mN\overline{c^2}$ ... (II.4)

The total mass of the gas is mN, so the density of the gas, $\rho = \frac{mN}{v}$

Hence, we have, $P = \frac{1}{3}\rho\overline{c^2}$ ... (II.5)

2.4. The temperature and Kinetic energy of a gas

Rewriting the kinetic theory equation (II.4),

$$Pv = \frac{1}{3}mN\overline{c^2} = \frac{2}{3}N \times \frac{1}{2}m\overline{c^2} = \frac{2}{3}N\epsilon$$

where $\frac{1}{2}m\overline{c^2} = \epsilon$, the mean kinetic energy of a single molecule.

For a mole of gas (volume, V), the number of molecules is N_0, Avogadro number. Hence

$$PV = \tfrac{2}{3}N_0\epsilon = \tfrac{2}{3}E \qquad \ldots\text{(II.6)}$$

where $E = N_0\epsilon =$ the kinetic energy of 1 mole of the gas. 'Kinetic energy' here always refers only to the translational type of motion of the molecules.

Now, from the gas laws, $PV = RT$, hence

$$\tfrac{2}{3}E = RT$$

Therefore, the K.E. of 1 mole, $E = \tfrac{3}{2}RT \qquad \ldots\text{(II.7)}$

For n moles: $E = (3/2)\,nRT$

Hence, the K.E. of one molecule, $\epsilon = \dfrac{E}{N_0} = \tfrac{3}{2}\dfrac{R}{N_0}T$

Remembering $R/N_0 = k$ (Boltzmann constant),

$$\epsilon = \tfrac{3}{2}kT \qquad \ldots\text{(II.8)}$$

The mean kinetic energy of a molecule in a gas is proportional to the absolute temperature of the gas. The mean K.E. does not depend upon the mass or nature of the gas molecules. When two gases are at the same temperature, the mean kinetic energy of their molecules will be the same.

Since $\epsilon = \tfrac{1}{2}m\overline{c^2} = \tfrac{1}{2}kT$

$\therefore \quad c = \sqrt{3kT/m} \qquad \ldots\text{(II.9)}$

i.e. root mean square velocity,

$$c = \sqrt{\frac{3RT}{mN_0}} = \sqrt{\frac{3RT}{M}} \qquad \ldots\text{(II.10)}$$

where M is the mol. wt. of the gas.

The velocity is proportional to the square-root of the absolute temperature and inversely proportional to the molecular mass. The heavier the molecule, lesser would be its velocity at a given temperature.

2.5. Derivation of the gas laws from the Kinetic Theory

The different gas laws which were empirically obtained can be easily derived from the kinetic theory.

(*i*) *Boyle's Law and Charles's Law*: We know,

$$Pv = \tfrac{1}{3}mN\overline{c^2} = \tfrac{2}{3}N \times \tfrac{1}{2}m\overline{c^2}$$

In a given mass (moles) of gas, the number of molecules N remains constant. Again, at a constant temperature, the mean kinetic energy of a molecule, $\tfrac{1}{2}mc^2$, remains constant. Hence, the right hand side is a constant.

$\therefore\ Pv =$ constant. This is *Boyle's Law.*

At a constant pressure, $v = \frac{2}{3}\frac{N}{P}\cdot\frac{1}{2}m\overline{c^2} = \frac{2}{3}\frac{N}{P}\frac{3}{2}kT = k'T$, which is *Charles's Law.*

(*ii*) *Avogadro's Law.* When equal volumes of two gases are taken at the same pressure and at the same temperature, we have

$$Pv = \tfrac{1}{3}m_1N_1\overline{c_1^2} = \tfrac{2}{3}N_1 \times \tfrac{1}{2}m_1\overline{c_1^2}$$

$$Pv = \tfrac{1}{3}m_2N_2\overline{c_2^2} = \tfrac{2}{3}N_2 \times \tfrac{1}{2}m_2\overline{c_2^2}$$

where (m_1, N_1, c_1) and (m_2, N_2, c_2) denote the mass, number and *r.m.s.* velocities of the molecules of the two gases respectively. Since the temperature is the same, the mean kinetic energy of the molecules of the two gases are equal, *i.e.*,

$$\tfrac{1}{2}m_1\overline{c_1^2} = \tfrac{1}{2}m_2\overline{c_2^2}. \qquad \text{Hence, } N_1 = N_2$$

i.e., equal volumes of the two gases at the same temperature and pressure contain the same number of molecules. This is Avogadro's Law.

(*iii*) *Dalton's Law of Partial pressures.* From the kinetic theory, we have the pressure of a gas, $P = \frac{1}{3}\frac{mN\overline{c^2}}{v} = \frac{2}{3}\frac{E}{v}$, or $E = \frac{3}{2}Pv$

where E = kinetic energy of the molecules.

If p_i, the partial pressure of the i-th component in a gas mixture, be the pressure it would exert if it occupied the total volume, v, then

$$p_i = \frac{2}{3}\frac{E_i}{v}, \quad \text{or} \quad E_i = \tfrac{3}{2}p_iv$$

In an ideal gas mixture, no energy is lost by collision, hence

$$E = E_1 + E_2 + \ldots + E_i + \ldots$$

$$\tfrac{3}{2}Pv = \tfrac{3}{2}p_1v + \tfrac{3}{2}p_2v + \ldots + \tfrac{3}{2}p_iv + \ldots$$

or

$$P = p_1 + p_2 + \ldots + p_i + \ldots$$

This is 'Dalton's Law of Partial pressures' (see Sec. 1.7).

(*iv*) *Graham's Law of Effusion.* We have,

$$P = \tfrac{1}{3}\rho\overline{c^2}$$

or

$$c = \sqrt{\frac{3P}{\rho}}$$

where c is the root-mean-square velocity. Now the root-mean-square velocity c is proportional to c_a, the average velocity of the molecules.

Hence,

$$c_a = k'\sqrt{\frac{3P}{\rho}}$$

When there is a fine orifice on the wall of the vessel containing the gas, the number of molecules which will effuse out is proportional to the average speed

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of the molecules c_a at any given temperature. That is, the rate of effusion r_e is proportional to c_a.

Hence,
$$r_e = k'.k'' \sqrt{\frac{3P}{\rho}}$$

So, *at a given pressure and temperature, the rate of effusion of a gas is inversely proportional to the square-root of its density*. This is Graham's Law.

2.6. Calculation of Kinetic energy and velocity of molecules

The kinetic energy and the root mean square velocity of molecules can be computed from equations, (II.8, 9). Some examples are given here.

1. Find out the kinetic energy of translation for 5 moles of a perfect gas at 0°C.

$$E = n \times \tfrac{3}{2}RT = 5 \times \tfrac{3}{2} \times 8.314 \times 273 \text{ joules}$$
$$= 17020 \text{ joules}$$

2. Assess the kinetic energy of a gm of NO-gas at 27°C.

mol. wt. of NO $= 30$; $\therefore$ 1 gm NO gas= $= \frac{1}{30}$ mole

$$\therefore E = n \times \tfrac{3}{2}\, RT = \tfrac{1}{30} \times \tfrac{3}{2} \times 8.314 \times 300 = 124.71 \text{ joules}$$

3. Calculate the r.m.s. velocity for (*a*) CO_2 molecules at 27°C and (*b*) deuterium molecules at N.T.P.

$$(a)\ \ c = \sqrt{\frac{3RT}{M}} = \sqrt{\frac{3 \times (8.314 \times 10^7) \times 300}{44}} = 41450 \text{ cm/sec}$$

$$(b)\ \ c = \sqrt{\frac{3RT}{M}} = \sqrt{\frac{3 \times (8.314 \times 10^7) \times 273}{4}} = 189800 \text{ cm/sec}$$
$$= 1.898 \text{ km/sec}$$

This illustrates higher velocities for lighter molecules. Further, the velocity is astonishingly high.

4. If the density of He-gas be 0.18 gm/litre at 760 mm. What is its molecular velocity?

$$\text{Since } P = \tfrac{1}{3}\rho \bar{c}^2\ \ ,\ c = \sqrt{\frac{3P}{\rho}},\ \ \rho = 0{\cdot}18 \times 10^{-3} \text{ gm/c.c.}$$

$$\text{Hence } c = \sqrt{\frac{3 \times 76 \times 13.6 \times 981}{0.18 \times 10^{-3}}} = 1.3 \times 10^5 \text{ cm/sec}$$

2.7. Distribution of molecular velocities (Maxwell)

The molecules in a gas are incessantly colliding and, in consequence, their velocities are constantly changing. The molecules do not all move with the same speed. At any instant, different velocities from very low to very high values exist. It would be interesting to know in what manner the molecules are distributed in the velocity spectrum from zero to very high magnitudes of speed, *i.e.* how many molecules have a low, how many have a very high, or how many molecules have a velocity of a given magnitude. This problem was satisfactorily solved from mathematical analysis for the first time by Maxwell (1860). For a gas at a given temperature, he derived a relation for the variation in the number of molecules with change in velocity. This relation known as 'Maxwell's law of distribution of velocities' is given as

$$\frac{1}{n}\frac{dn_c}{dc} = 4\pi\left(\frac{M}{2\pi RT}\right)^{3/2} e^{\frac{-Mc^2}{2RT}} c^2 \tag{II.11}$$

where n is the total number of molecules and n_c is the number of molecules having a velocity, c.

The expression on the left-hand side of eqn. (II.11), gives the fraction of the total number of molecules having velocity between c and $c + dc$. The implication of this relation is more clearly understood from its graphical representation, as in Fig. II-2. The fraction of molecules $\left(\frac{1}{n}\frac{dn_c}{dc}\right)$ is plotted against velocity c, the temperature (T) remaining constant. With increase in velocity, the curve rises gradually, reaches a maximum and then slopes downwards. The curves would be different for different temperatures as also for different gases, but the nature would be the same.

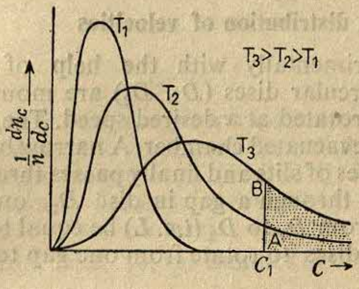


Fig. II.2. Distribution function at different temperatures $T_1 < T_2 < T_2$

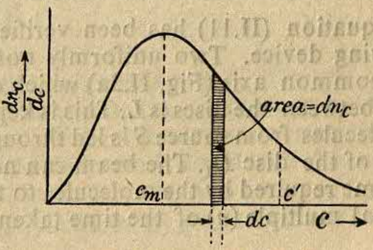


Fig. II.3. Maxwell's distribution function

It indicates that the percentage of molecules having very high or very low velocities is indeed quite small. The maximum of the curve indicates the velocity possessed by the largest group of molecules. This velocity which is acquired by more molecules than with any other velocity is called the **most probable velocity** denoted by c_m.

With increase in temperature, the curves are flattened, *i.e.*, the velocities are more widely distributed. The value of the most probable velocity also increases.

To find out the number of molecules having velocities, between 400 *m/sec* and 410 *m/sec* (say), the ordinates at these two velocity-points may be drawn (see Fig. II-3). The area within these two ordinates divided by the total area under the curve would give us the required fraction of the total number of molecules having the prescribed velocity-range. Let us suppose, this fraction is 1.5 percent. It means that at this temperature, always 1.5 percent of the molecules will have velocity approximating 400 *m/sec*, though the molecules having that velocity would be different at different moment.

Previously, two kinds of velocities for gas molecules—root mean square and average velocity—have been defined. Another kind, namely, most probable velocity is defined now. From appropriate solutions of the Maxwell's distribution equation (II.11), the following expressions for different types of velocities have been derived.

(*a*) Root mean square velocity : $c = \sqrt{\frac{3RT}{M}} = 1.58\times10^4\sqrt{\frac{T}{M}}$ cm sec^{-1}

(*b*) Average velocity : $c_a = \sqrt{\frac{8RT}{\pi M}} = 1.45\times10^4\sqrt{\frac{T}{M}}$ cm sec^{-1}

(*c*) Most probable velocity : $c_m = \sqrt{\frac{2RT}{M}} = 1.29\times10^4\sqrt{\frac{T}{M}}$ cm sec^{-1}

...(II.12)

Hence $c : c_a : c_m = 1.22 : 1.13 : 1$

Example: Calculate the most probable and average velocity of N_2 molecules at 15°C.

$$c_m = 1.29 \times 10^4 \sqrt{288/28} = 4.14 \times 10^4 \text{ cm sec}^{-1}$$
$$c_a = 1.45 \times 10^4 \sqrt{288/28} = 4.66 \times 10^4 \text{ cm sec}^{-1}$$

Experimental Verifcation of Maxwell distribution of velocities

The equation (II.11) has been verified experimentally with the help of the following device. Two uniformly notched circular discs (D_1, D_2) are mounted on a common axis (Fig. II.3a) which can be rotated at a desired speed. The distance between the discs is L. This is kept in an evacuated chamber. A narrow beam of molecules from source S is led through a series of slits and finally passes through a gap of the disc D_1. The beam can next pass through a gap in disc D_2, only if the time required by the molecules to travel from D_1 to D_2 (*i.e.* L) be equal to an integral multiple (n) of the time taken by the discs to rotate from one gap to the next. Under such conditions, the velocity of the gas molecules would be, $v = L.x.w/2\pi n$, where w is the angular velocity of rotation and x is the number of notches in the disc. The molecules emerging from disc D_2 enter into a radiometer whose deflection gives the number of molecules having the said velocity. The number is thus known. In subsequent observations, the speed of rotation is gradually changed and the number of molecules having different speeds are known. The velocity distribution is thus experimentally found out and this satisfies the curve given in Fig. II.3.

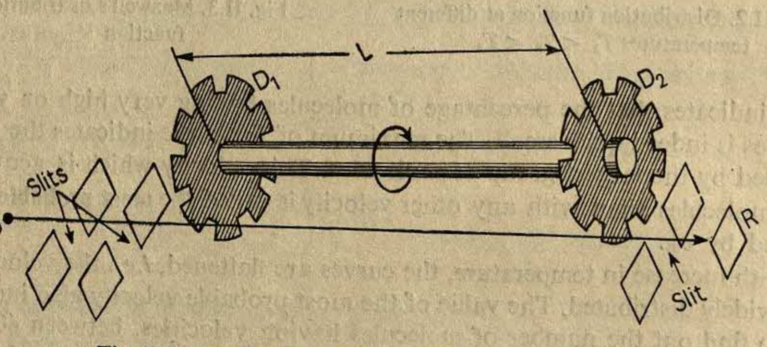


Fig. II.3a. Verification of Maxwell distribution of velocities

2.8. Collision Number

The number of molecules of a gas in any given volume, say 1 c.c., is extremely large. Due to their incessant motion there would be enormous number of collisions. It would be of interest to find out the number of collisions occurring in every c.c. of the gas. Suppose there are n molecules present per c.c. in a gas having average velocity c_a. Assume that the radius of each molecule is r and its diameter is σ $(= 2r)$.

A selected molecule P will collide with the molecule Q when the distance between their centres is σ. Imagine a sphere of radius σ around the centre of P. Any other molecule whose centre would come within this sphere will obviously collide with the given molecule P. Since the molecule travels a distance c_a in one second, the volume of the colliding space that would be swept away by it in one second is $\pi\sigma^2 \times c_a$ (Fig. II.4). If all the other molecules were stationary, the number of molecules with which the selected molecule P would collide is $\pi\sigma^2 c_a n$.

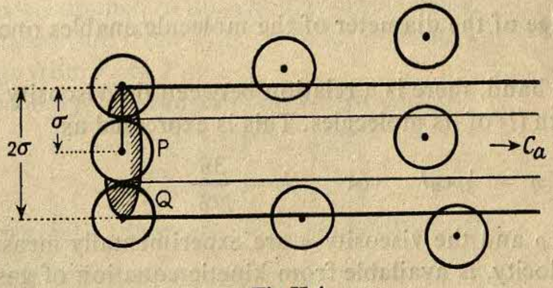


Fig II.4

But the molecules are not stationary, hence a correction factor $\sqrt{2}$ has been introduced. So, the number of collisions (Z_1) suffered by a molecule per second,

$$Z_1 = \sqrt{2}\pi\, \sigma^2 c_a n \qquad \ldots \text{(II.13)}$$

This is true for each molecule. Hence, the total number of collisions for n molecules occurring per c.c. is

$$Z_{AA} = \tfrac{1}{2}n \times \sqrt{2}\pi\sigma^2 c_a n = \frac{1}{\sqrt{2}}\pi\sigma^2 c_a n^2 \qquad \text{(II.14)}$$

The factor $(\frac{1}{2})$ is necessary as each collision involved two molecules, otherwise each collision would be counted twice.

Example : Calculate the number of bimolecular collisions per c.c. per second of N_2 gas at 1 atm and 25°C. $(\sigma = 3.74\text{A}^\circ)$

Using eqn. (II.12), c_a is found to be 4.8×10^4 cm/sec.

$$n = \text{number of molecules/c.c.} = \frac{6.02 \times 10^{23}}{22414} \times \frac{273}{298} = 2.46 \times 10^{19}$$

$$\text{Hence, number of collisions per c.c.} = \frac{1}{\sqrt{2}}\pi\sigma^2 c_a n^2$$

$$= \frac{1}{\sqrt{2}} \times (3.14)(3.74 \times 10^{-8})^2 \times (4.8 \times 10^4)(2.46 \times 10^{19})^2 = 8.98 \times 10^{28}$$

It is indeed an enormous number.

2.9. Mean free path

The average distance covered by a molecule between two successive collisions is called the mean free path and is denoted by l. In one second, a molecule travels a distance c_a and it suffers Z_1 collisions (eqn. II.13). That is the mean free path,

$$l = \frac{\text{average velocity of the molecules}}{\text{number of collisions per second}} = \frac{c_a}{Z_1}$$

$$\text{or } l = \frac{c_a}{\sqrt{2}\pi\sigma^2 c_a n} = \frac{1}{\sqrt{2}\pi\sigma^2 n} \qquad \text{...(II.15)}$$

Hence a knowledge of the diameter of the molecule enables one to compute the mean free path.

On the other hand, there is a relation between the viscosity (η) of a gas and the mean free path (l) of its molecules. This is expressed as

$$\eta = \tfrac{1}{3}\rho c_a l \quad \text{or} \quad l = \frac{3\eta}{\rho c_a} \qquad \text{...(II.16)}$$

Both the density ρ and the viscosity η are experimentally measured. The value of c_a, average velocity, is available from kinetic equation of gases (eqn. II. 12). So, the mean free path can be evaluated. Some of the mean free paths at N.T.P. are

gas	H_2	He	O_2	N_2
l	1.1×10^{-5}	1.8×10^{-5}	6.4×10^{-5}	5.95×10^{-5} cm

2.10. Heat capacity of gases

The quantity of heat required to raise the temperature of a body by one degree is called its 'heat-capacity'. Usually the rise in temperature is measured in centigrade degree and the heat-capacity in joules or calories. Obviously the heat capacity will depend upon the amount of material present in the system. The heat-capacity for a *mole* of a substance is called its 'molar heat capacity', or simply *heat capacity of the substance.*

The magnitude of heat-capacity depends on the pressure and the volume, especially so in the case of gases. Heat-capacity of gases are generally expressed under two specified conditions.

(*i*) *Heat capacity at constant volume* is defined as the amount of heat required to increase the temperature of one mole of gas by 1°C, the volume of the gas being kept constant during heating. It is denoted by C_v.

(*ii*) *Heat capacity at constant pressure* is defined as the amount of heat required to increase the temperature of one mole of gas by 1°C, the pressure of the gas being kept constant during heating. It is denoted by C_p.

If the quantity of the gas be 1 gm instead of 1 mole, then the amounts of heat required are called specific heats of the substance. If c_v and c_p denote the specific heats of the gas, then

$$C_p = Mc_p \quad \text{and} \quad C_v = Mc_v$$

where M is the mol. wt. of the gas.

Heat-capacities from the Kinetic Theory : When heat is supplied to a gas for raising its temperature, it is utilised in three possible ways:

(*a*) to increase the kinetic energy of translation of the molecules

(*b*) to increase the intra-molecular energies of the molecule such as vibrational, rotational energies, and

(*c*) to supply the energy required for the work of expansion, if any, during the rise in temperature.

(*i*) Let us take 1 mole of a gas at a temperature (T_1°K) at a pressure P_1 having a volume V, in a cylinder (Fig. II. 5).

Suppose heat is supplied to this gas *at constant volume* to increase its temperature from T_1°K to T_2°K, when pressure would change from P_1 to P_2.

From kinetic theory, the translational kinetic energy

$$E_1 = \tfrac{3}{2}P_1V = \tfrac{3}{2}RT_1$$

$$E_2 = \tfrac{3}{2}P_2V = \tfrac{3}{2}RT_2$$

$\therefore$ Increase in kinetic energy, $E_2 - E_1 = \tfrac{3}{2}R(T_2 - T_1)$.

$\therefore$ For 1° rise in temperature, $\triangle E = \tfrac{3}{2}R$

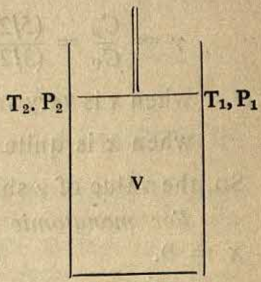


Fig. II.5.

Further, let us suppose the increase in intra-molecular or internal energy for 1°C rise in temperature is x.

Since the gas is kept at constant volume ($\triangle V = 0$), so no work is involved in expansion-work.

These energies have been derived from the heat supplied.

Hence $$C_v = \tfrac{3}{2}R + x \qquad \text{(II.17)}$$

(*ii*) Again, let us supply heat to the same one mole of gas *at a constant pressure P*, when its temperature rises from T_1^0 to T_2^0K and volume from V_1 to V_2.

(*a*) The translational kinetic energies are $E_1 = \tfrac{3}{2}RT_1$ and $E_2 = \tfrac{3}{2}RT_2$

$$\therefore\ E_2 - E_1 = \tfrac{3}{2}R(T_2 - T_1)$$

For 1°C rise in temperature, $\triangle E = \tfrac{3}{2}R$

(*b*) The increase in intra-molecular energy for 1°C rise in temperature is x, as before.

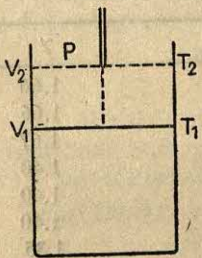


Fig. II-6.

(*c*) During the heating, the gas has expanded as the pressure is constant. This needed work (w) which was also obtained at the expense of heat supplied.

$$w = P(V_2 - V_1) = RT_2 - RT_1 = R(T_2 - T_1)$$

$$= R, \text{(when increase in temperature is 1°C)}$$

$\therefore$ The total energy involved for 1°C rise in temperature at constant pressure is $\tfrac{3}{2}R + x + R$, *i.e.*

$$C_p = \tfrac{3}{2}R + R + x = \tfrac{5}{2}R + x \qquad \text{(II.18)}$$

Hence C_p will be always higher than C_v of a gas.

Difference in the heat capacities C_p and C_v : For any gas,

$$C_p = \tfrac{5}{2}R + x \quad \text{and} \quad C_v = \tfrac{3}{2}R + x$$

Hence $\quad C_p - C_v = R = 8.314 \text{ joules} = 1.987 \text{ calories}$

For approximate calculation, $C_p - C_v \approx 2$ cal.

Heat capacity ratio, $C_p/C_v = \gamma$: The ratio of the heat capacity at constant pressure to that at constant volume of a gas is denoted by γ, sometimes called 'Poisson ratio'.

$$\gamma = \frac{C_p}{C_v} = \frac{(5/2)R + x}{(3/2)R + x} = \frac{5 + x}{3 + x}, \quad \text{(taking } R \approx 2\text{cal)} \qquad \text{(II.19)}$$

when x is very small, $\quad Lt_{x \to 0} \quad \gamma = \frac{5}{3} = 1.66$

when x is quite large, $\quad Lt_{x \to \infty}, \quad \gamma = 1$

So, the value of γ shall remain between 1.66 and 1.00

For monatomic gases, there is no internal vibration or rotation, hence $x = 0$.

So, $\qquad \gamma \text{ (for monatomic gases)} = \frac{5}{3} = 1.66$

All monatomic gases like He, Ne, A, Hg-vapour, etc. have γ-values 1.66.

For diatomic gases, $\gamma = 1.40$, for triatomic gases, $\gamma = 1.31$. With increase in atomicity x increases and γ-values of gases decrease. Heat capacities and γ-values of some gases given here would confirm this.

MOLAR HEAT CAPACITIES IN CALORIES

(P = 1 atm, T = 298°K)

Gas	C_p	C_v	γ
Argon	4.97	2.98	1.66
Helium	4.97	2.98	1.66
Mercury	5.0	3.0	1.67
Hydrogen	6.85	4.86	1.40
Nitrogen	6.96	4.97	1.40
Oxygen	7.03	5.03	1.40
Chlorine	8.10	6.00	1.35
Nitric oxide	7.10	5.10	1.39
Carbon dioxide	8.83	6.80	1.30
Sulphur dioxide	9.65	7.50	1.29
Nitrous oxide	9.08	7.03	1.29
Water	8.67	6.47	1.34
Methane	8.50	6.50	1.31
Acetylene	10.45	8.40	1.24
Ethane	10.25	8.20	1.25

2.11. Degrees of Freedom: Heat capacity

The mean square velocity of the molecules,

$$\bar{c}^2 = \bar{c}_x^2 + \bar{c}_y^2 + \bar{c}_z^2$$

where $\overline{c_x^2}$, $\overline{c_y^2}$, $\overline{c_z^2}$ are the mean squares of the component velocities in three mutually perpendicular directions. These three mean square velocities must be equal to one another, as otherwise there would be greater concentration or higher density of molecules in one side of the gas system, which is not so. Hence,

$$\overline{c_x^2} = \overline{c_y^2} = \overline{c_z^2}, \text{ i.e. } \overline{c^2} = 3\overline{c_x^2}$$

Now, the kinetic energy of translation of a molecule,

$$\epsilon_{tr} = \tfrac{1}{2}m\overline{c^2} = \tfrac{1}{2}m\overline{c_x^2} + \tfrac{1}{2}m\overline{c_y^2} + \tfrac{1}{2}m\overline{c_z^2}$$

$$= \tfrac{3}{2}m\overline{c_x^2} = 3\epsilon_x$$

Since $\epsilon_{tr} = \tfrac{3}{2}kT, \quad 3\epsilon_x = \tfrac{3}{2}kT$

Or $\epsilon_x = \tfrac{1}{2}kT$

Similarly $\epsilon_y = \tfrac{1}{2}kT, \quad \epsilon_z = \tfrac{1}{2}kT$

That is, the kinetic energy of translation of the molecule is equally distributed along three components of motion of the particle.

If there be N molecules in a system, the system can be described by three co-ordinates for each particle or there will be a total of $3N$ co-ordinates. At any instant, any of the components can vary by any amount, the system is said to possess three independent components of motion or three *degrees of freedom.* We have just seen that the energy associated with each translation degree of freedom is $\tfrac{1}{2}kT$ per molecule, *i.e.*, the energy is equally distributed among the degrees of freedom. The energy along any degree of freedom is proportional to the square of a velocity component or a positional co-ordinate.

Extending this idea also to other forms of energy possessed by the molecules, Maxwell and Boltzmann proposed the **law of equipartition of energy** which states:

The total kinetic energy of a molecule is equally distributed along the various degrees of freedom, each degree of freedom having energy $\tfrac{1}{2}kT$ per molecule.

Monatomic gas molecules are concerned with translational energy only with three degrees of freedom. Hence.

$$\text{kinetic energy, } \epsilon = 3 \times \tfrac{1}{2}kT = \tfrac{3}{2}kT \text{ per molecule}$$

$$E = \tfrac{3}{2}RT \text{ per mole}$$

But diatomic molecules have rotational and vibrational energies besides translational energy; each of these have degrees of freedom. Diatomic molecules have 3 translational, 2 rotational and 2 vibrational degrees of freedom. Hence,

$$\text{Total energy } \epsilon = 3 \times \tfrac{1}{2}kT + 2 \times \tfrac{1}{2}kT + 2 \times \tfrac{1}{2}kT = \tfrac{7}{2}kT \text{ per molecule}$$

$$E = \tfrac{7}{2}RT \text{ per mole.}$$

Heat capacity, C_v. (*i*) In monatomic gases, then

$$C_v = E_{T+1} - E_T = \tfrac{3}{2}R(T+1) - \tfrac{3}{2}RT$$

$$= (3/2)R = 3 \text{ cal. per mole (approx.)}$$

This is indeed the value experimentally observed (Table p. 28)

(*ii*) For diatomic gases, we have

$$C_v = E_{T+1} - E_T = \tfrac{7}{2}R(T+1) - \tfrac{7}{2}RT = \tfrac{7}{2}R$$

$$= 7 \text{ cal per mole (approx.)}$$

Experimentally the value is less under ordinary conditions as excitation of the vibrational energy is almost absent.

2.12. Determination of heat-capacity ratio, γ

There are several methods for the determination of heat-capacity ratio, γ. Only two methods are mentioned here.

(*i*) *From adiabatic expansion*: When a change of a system occurs without any variation of temperature during the change it is called an *isothermal change*. On the other hand, a system may be thermally insulated from the surroundings and then the change is carried out such that no heat energy can enter into or flow out of the system (the temperature may alter). Such a change is called an *adiabatic change*. With the help of an adiabatic expansion of a gas, its γ-value can be ascertained.

The relation between P and V for 1 mole of gas in an isothermal change is given by $PV = RT$ (Boyle's Law). But in an adiabatic expansion of the same the relation is (see Sec. 8.14)

$$PV^{\gamma} = \text{constant}$$

Partington used this relation to obtain γ in the following way:

A very large copper globe (about 130 litres capacity) was filled up with the gas at a pressure somewhat higher than the external atmospheric pressure. The vessel is provided with a manometer and a control-valve. The temperature of the gas could be ascertained from a sensitive *Pt*-resistance thermometer thurst inside the globe (Fig. II.7)

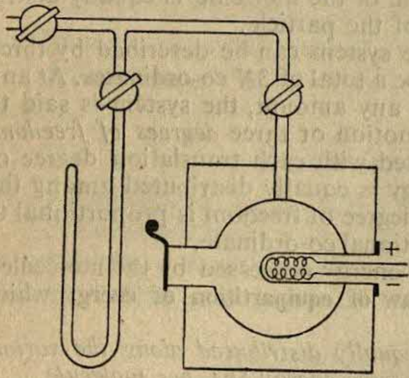


Fig. II-7

Suppose initially the temperature is T_1, pressure P_1 and molar volume of the gas V_1. The valve is opened for a short while when the gas expands and a portion goes out. The valve is immediately closed. The pressure immediately falls to that of the external pressure P. The pressures P_1 and P, as also the temperatures T_1 and T are noted. Let the molar volume of the gas under the pressure P and final temperature T be V. Then,

from the kinetic theory, $P_1V_1 = RT_1$ and $PV = RT$

i.e.,
$$\frac{V_1}{V} = \frac{PT_1}{P_1T}$$

Again, for the adiabatic expansion, $P_1V_1^{\gamma} = PV^{\gamma}$

i.e.,
$$\frac{V_1}{V} = \left(\frac{P}{P_1}\right)^{\frac{1}{\gamma}}$$

Hence
$$\frac{PT_1}{P_1T} = \left(\frac{P}{P_1}\right)^{\frac{1}{\gamma}}$$

or
$$\gamma = \frac{\log P_1 - \log P}{(\log P_1 - \log P) - (\log T_1 - \log T)}$$

γ is thus known.

(*ii*) *From the velocity of sound*: *Kundt's method*: The velocity of sound v in a gas is given by Laplace's equation,

$$v = \sqrt{\frac{\gamma P}{d}},$$ where P and d are the pressure and density of the gas.

If d_1, d_2 be the densities of two gases in which the respective velocities are v_1 and v_2, at the same pressure,

$$\frac{v_1^2}{v_2^2} = \frac{\gamma_1 d_2}{\gamma_2 d_1} \quad \text{or} \quad \frac{v_1^2\lambda_1^2}{v_2^2\lambda_2^2} = \frac{\gamma_1 d_2}{\gamma_2 d_1}$$

since velocity, v = frequency × wavelength = $\nu \times \lambda$. If sound of the same frequency is passed through the two gases, $\nu_1 = \nu_2$, so

$$\frac{\lambda_1^2}{\lambda_2^2} = \frac{\gamma_1 d_2}{\gamma_2 d_1} \quad \text{or} \quad \gamma_1 = \frac{\lambda_1^2 d_1}{\lambda_2^2 d_2}\gamma_2$$

If the second gas be a known one, γ_2 is known.

Kundt's apparatus consists of a glass tube (B) about a metre long closed by corks at the two ends (A and C). A little lycopodium powder is spread inside the tube. Through the cork at A is inserted a metal rod. Through the cork at C is inserted a rod which flattens into a disc inside. The tube is filled with the gas under investigation. The rod in A is now stroked with a stretched string or wet-cloth, setting the rod into vibration. The disc at the other end is adjusted in such a way, that length between A and C becomes an exact multiple of λ. This would make the lycopodium powder to settle into small heaps at definite intervals, where the vibration is least (at the nodes). The distance (l_1) between two consecutive heaps is measured, which is half the wavelength ($\lambda_1/2$) of the sound waves.

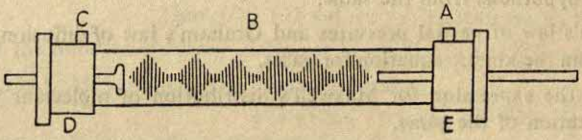


Fig II–8. Kundt's apparatus

The experiment is repeated with a known gas and the corresponding distance l_2 (= $\lambda_2/2$) is also measured.

Then $$\gamma_1 = \frac{\lambda_1^2 d_1}{\lambda_2^2 d_2}\gamma_2 = \frac{l_1^2 d_1}{l_2^2 d_2}\gamma_2 \qquad \text{. . . (II.20)}$$

The densities of the two gases must be separately ascertained. Hence γ_1 heat capacity ratio is known.

Problem: The specific heats at constant volume and at constant pressure of a gas are 0.075 and 0.125 respectively. Find the molecular weight of the gas.

$$M(c_p - c_v) = R = 1.987$$

$$\therefore \qquad M = \frac{1.987}{0.125 - 0.075} = 39.7$$

Problem: In a Kundt's experiment for γ-determination,

	air	nitrogen
λ	112.12	114.02
d	1.2928	1.2507

these experimental values were recorded. (γ_{air} = 1.405). Find γ-value for nitrogen. What is its atomicity?

From equation (II.20), we have

$$\gamma_{N_2} = \frac{(114.02)^2 \times 1.2507}{(112.12)^2 \times 1.2928} \times 1.405 = 1.406$$

Since $\gamma \approx 1.4$, hence the nitrogen molecule would be diatomic.

EXERCISES

I

1. Explain clearly root mean square, average and most probable velocity of gas molecules. How are these related? Cite an example to illustrate the importance of the r.m.s. velocity.

2. Deduce the kinetic equation for gases, $PV = \frac{1}{3}mnc^2$ for an ideal gas mentioning the postulates on which it is based.

3. How is density of a gas related to its pressure? Will the same relation hold true for the vapour-density?

4. Establish the equation of state for ideal gases from the kinetic theory equation and also deduce Avogadro's hypothesis from the same.

5. State Dalton's law of partial pressures and Graham's law of diffusion. Show how these can be arrived at from the kinetic equation for gases.

6. Write down the expression for Maxwell's distribution of molecular velocities. Give a qualitative interpretation of the same.

7. Write notes on: (*a*) mean free path (*b*) collision number (*c*) adiabatic change.

8. Why are heat capacities at a constant volume and at a constant pressure different for a gas. How are these two related?

9. Why $(C_p - C_v)$ is the same for all gases but their C_p/C_v-values are not always the same? Give a brief outline of a method for the determination of γ ?

10. Justify or correct the following statements:

   (*a*) The average momentum of a gas molecule is proportional to $\sqrt{T}$.

   (*b*) At a given temperature, the average velocities of molecules of all gases would be the same.

   (*c*) The average velocity of a deuterium molecule will be half of the average velocity of a hydrogen molecule.

II

11. Find out the (*i*) r.m.s. (*ii*) average and (*iii*) most probable velocities of the O_2-molecules at 0°C. **[Ans.** (*i*) 4.613×10^4 (*ii*) 4.252×10^4 (*iii*) 3.765×10^4 cm/sec]

12. What is the average velocity of (*i*) H_2-molecules at 27°C and (*ii*) O_2-molecules at 25°C. **[Ans.** (*i*) 18.61×10^4 (*ii*) 4.44×10^4 cm/sec]

Note that the speed of the H_2-molecules is 4-times faster than that of the O_2-molecules.

13. At what temperature, will the molecules of oxygen have the same velocity as that of nitrogen at 7°C? **[Ans.** 320°K]

14. If the density of oxygen be 1.44 gm/litre at normal pressure. Compute its molecular velocity. **[Ans.** 4.592×10^4 cm/sec.]

15. (*a*) Two moles of Neon occupy a volume of 5 litres at a pressure of 10 atm. Calculate its kinetic energy. **[Ans.** 75 lit-atm.]

(*b*) Calculate the average kinetic energy of a CO_2 molecule at 15°C in calories. (C.U. '82) **[Ans.** 2.86×10^{-21} cal]

16. Find out the kinetic energy of : (*i*) 5 moles of an ideal gas at 0°C, (*ii*) one gm of CO_2 gas at 27°C, (*iii*) one litre of Helium at N.T.P. **[Ans.** (*i*) 1.72×10^4 joules (*ii*) 20.45 cal (*iii*) 1.54×10^2 joules]

17. (*i*) The specific heat of argon ($M = 40$) at constant volume is 0.075 what is the atomicity of its molecules? (*ii*) Estimate the molecular weight of a gas whose specific heats at constant volume and constant pressure are 0.15 and 0.25. **[Ans.** (*i*) 1 (*ii*) 200]

18. From a sample of Ra 1.82×10^{17} α-particles were expelled which on standing gave 7.34×10^{-3} c.c. of helium gas measured at 19°C and 745 mm pressure. Calculate the Avogadro number. **[Ans.** 6.06×10^{23}]

19. A gaseous mixture containing 0.7 gm nitrogen and 11200 c.c. O_2 at STP is contained in a 10-liter flask at 27°C. Calculate the partial pressure of each gas and also the total pressure. (Punjab, '76) **[Ans.** $p_{N_2} = 0.062$, $p_{O_2} = 1.23$, $P = 1.292$ atm]

20. Calculate: (*i*) most probable velocity in km per sec for H_2 molecules at 27°C (*Andhra*, '74), (*ii*) R.M.S. velocity of an SO_2 molecule at 0°C (*Delhi*, '76), (*iii*) the kinetic energy of two moles of CO_2 at 27°C. (*Delhi*, '74).

[Ans. (*i*) 1.573 km sec^{-1} (*ii*) 32640 cm sec^{-1} (*iii*) 7428.6 joules]

21. Calculate the number of binary collisions in a CO gas at 27°C and 250 mm pressure (diameter $\sigma = 3.19\text{Å}$). Also estimate the mean free path.

[Ans. $Z_{AA} = 1.395 \times 10^{28}$; $l = 2.75 \times 10^{-5}$ cm]

22. At NTP, the mean free path in the hydrogen gas is 1.78×10^{-5} cm and the velocity of the hydrogen molecule is 1.83 km/sec. Calculate the number of bimolecular collisions per c.c. per sec. **[Ans.** 6.2×10^{28}]

23. The specific heats at const. volume and at const. pressure of a gas are 0.153 and 0.198 respectively. Calculate the mol. wt. of the gas. **[Ans.** 44.4]

24. The rates of diffusion of CO_2 and ozone are in the ratio 0.58 : 0.342. Calculate the mol. wt. of ozone assuming that of CO_2. (Cal. 1970) **[Ans.** 50.38]

25. Air contains 78 % N_2 and 21 % O_2 by volume at N.T.P. Calculate their partial pressures.

[Ans. $P_{O_2} = 159.6$ mm, $P_{N_2} = 592.8$ mm]

CHAPTER 3

REAL GASES

3.1. Ideal and Real gases

In the last century, Andrews, Amagat, Regnault and others made extensive studies of the behaviour of many gases like H_2, O_2, CO_2, N_2, CH_4, etc. It was observed that these gases follow the kinetic equation, $Pv = \frac{1}{3}mnc^2$ (and hence $Pv = nRT$), only approximately. At higher pressures and at very low temperatures, these gases depart considerably widely from the requirements of this equation. An *ideal gas* has therefore been defined as one which would strictly obey the kinetic gas equation ($Pv = \frac{1}{3}mnc^2$) and thus conform to all the postulates of the theory. The gases, which we actually deal with, are hence ***non-ideal*** or *real gases.*

3.2. Deviations from ideal behaviour

The departure from ideal behaviour in real gases has been observed in different types of investigation. A few of these are mentioned here.

(*i*) *Variation of Pv with pressure*: At a constant temperature, for a given mass of gas, Pv should remain constant even if pressure is varied. Hence Pv plotted against P should be a straight line parallel to the P-axis. Amagat studied this for many gases at different constant temperatures; the experimental $Pv-P$ curves are of the nature as shown in Figs. (III. 1 and 2). At very low pressures (below 1 atm.) the plots of $Pv-P$ are linear but not parallel to the P-axis (Fig. 1). For higher pressures with wide variations, $Pv - P$ isothermals are as given in Fig 2. The Pv-value first diminishes, reaches a minimum and then rises, forming a cup, with increase in pressure. There is thus a considerable departure from the ideal behaviour.

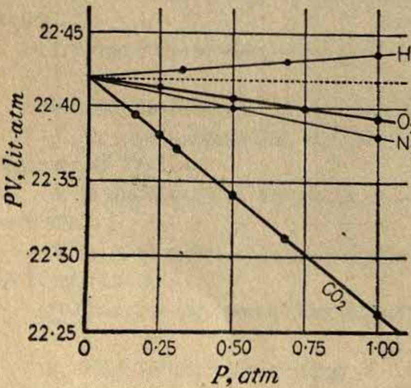


Fig. III.1
Pv-P isothermals at low pressures

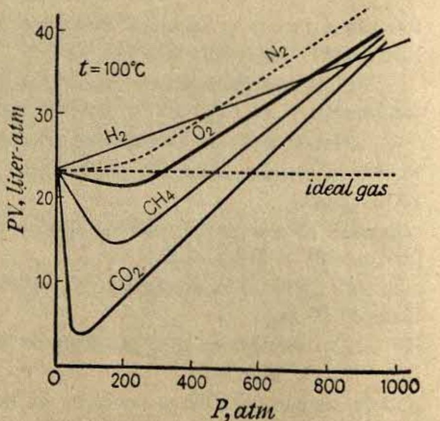


Fig. III.2
Pv-P isothermals at higher pressures

The curves in Fig. 2 reveal that at low pressures, the gases are more compressible than the ideal gases. At high pressures, the gases become less compressible than the ideal gases.

(*ii*) *Variation of P with v*: From the Boyle's law, the plot of pressure against volume (P-v plot) at a constant temperature should be a rectangular hyperbola. The historically famous experiments of Andrews on the study of P-v relations with carbon dioxide gas revealed considerable departure from the Boyle's law. The P-v curves were found to be as those represented in Fig. III. 3. At higher temperatures, the isotherms look similar to those for ideal gases, though not strictly rectangular hyperbolas. At lower temperatures, the curves seem to consist of three parts, as at 13.1°C it is formed of PQ, QR and RS. We shall discuss these Andrew's curves in detail later. These show that real gases deviate from ideal behaviour.

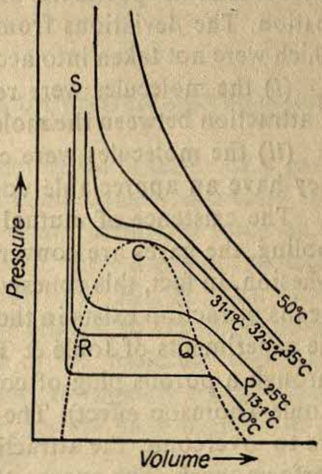


Fig. III.3
P–v curves for CO_2

(*iii*) On the kinetic theory Avogadro's law was based. At a constant temperature and pressure, one mole of any gas must have the same volume. Experimental values for the volume of a mole of different gases as recorded below show that the volume is not constant. That is, $Pv = nRT$ is only approximately true.

MOLAR VOLUMES OF DIFFERENT GASES (N.T.P.)

Gas	CO_2	NH_3	O_2	N_2	H_2	Ideal value
Volume in litres	22.264	22.084	22.394	22.405	22.427	22.414

(*iv*) The coefficient of thermal expansion (α) is defined as the rate of change of volume per unit-volume with change in temperature, at constant pressure, *i.e.*,

$$\alpha = \frac{1}{v}\left(\frac{\partial v}{\partial T}\right)_P \qquad \text{(III.1)}$$

For an ideal gas, $v = \frac{nRT}{P}$, hence $\left(\frac{\partial v}{\partial T}\right)_P = \frac{nR}{P}$

Hence
$$\alpha = \frac{1}{v}\cdot\frac{nR}{P} = \frac{nR}{nRT} = \frac{1}{T} \qquad \text{(III.2)}$$

That is, the coefficient of thermal expansion will be a function of temperature only and will thus be the same for all gases. But the α-values of different gases are found to be different, contrary to the expectations from the ideal gas laws.

3.3. Causes of deviation from ideal behaviour

Now that the ideal gas laws are found to be only approximate, it is obvious that some of the postulates of the kinetic theory are inadequate and need modification. The deviations from the ideal laws are primarily due to two factors which were not taken into account or ignored in the theory:

(*i*) the molecules were regarded as perfectly elastic, the existence of forces of attraction between the molecules were ignored.

(*ii*) the molecules were considered as point masses having no volume but they have an appreciable volume.

The existence of mutual force of attraction can be easily understood. On cooling, the gases are converted into liquids when the molecules exhibit strong cohesion. In fact, this cohesive force plays an important part in liquefaction. This means attraction exists in the gas phase also. A more clear evidence comes from the experiments of Joule & Thomson. When a stream of gas is allowed to pass through a porous plug of cotton or earthenware, there is a fall of temperature (Joule-Thomson effect). The only explanation is that the outgoing molecules are to overcome the attraction of the molecules from behind and thus have to perform work. The energy thus spent causes a lowering of temperature. In an ideal gas, there is no attractive force between the molecules and no cooling would be expected.

A portion of the volume (V) of a gas is indeed occupied by the bodies of the molecules. This volume may be insignificant if the pressure is very low, when V is very large. But at ordinary pressures, the space occupied by the molecules is nearly 0.1 percent of the volume (V) of the gas and is not negligible.

Due to intermolecular attraction, the number of impacts a molecule would make on the wall would be less than what it could if it were free from attraction. This is true for each molecule. As a result, the observed pressure (P) will be less than the pressure (P_0) the gas would have if it were ideal and there were no intermolecular attraction. If the decrease in pressure be denoted by p', then the ideal pressure would be $(P + p')$.

It is also easily seen that the space available for the motion of the molecules is less than the volume the gas occupies. Suppose a molecule is moving at right angles to the opposite walls (Fig. III.4) of the containing vessel whose distance is l. If the molecules were point masses, the distance to be travelled by a molecule between two successive impacts on the same wall would be $2l$. But the molecules have dimensions, and therefore the distance actually covered by the molecules is $(2l—\sigma)$, where σ is the diameter of the molecule. This is true for all molecules. As a result, the space for free motion of the molecules would be measurably reduced. Suppose v' denotes the reduction in space, then the true volume for motion of the molecules would be $V—v'$, where V is the volume of the gas. We may then write the equation of state, corrected for the volume and the pressure, of a real gas in the form

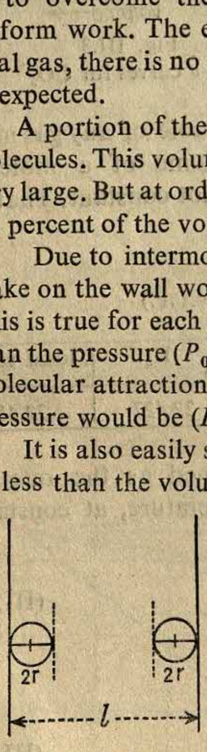


Fig. III.4

$$(P + p')\ (V—v') = RT \qquad \text{(for 1 gm-mole)}$$

Many attempts have been made during the last hundred years to modify the ideal gas equation and change it into a form which would represent *P-V-T* relations of real gases. Corrections had to be introduced both for the pressure as well as for the volume. Of these attempts, the most useful and universally accepted is that proposed by van der Waals (1873).

3.4. van der Waals Equation

van der Waals introduced the two corrections for pressure and volume into the ideal gas equation in the following way:

(*a*) *Pressure correction, p'*: A molecule present in the interior of a gas is surrounded on all sides by other molecules. It is being equally attracted from all directions and in consequence there is no resultant attractive force on the molecule. But when it is just going to strike the wall, there are more molecules towards the interior away from the direction of the wall (Fig. III. 4a). Hence, the molecule is attracted more strongly towards the interior by the larger number of molecules in the bulk. As a result, the motion of the molecule towards the wall is retarded. Due to this retardation, the number of impacts on the wall by this molecule per second will be less than what it should have been if the gas were ideal and there were no attraction between the molecules. The pressure depends upon the number of impacts per second on the wall. Hence, with the real gas, the pressure would be less than that it would be if the gas were ideal. The measured pressure is less than the ideal pressure.

Let there be a mole of gas in volume *V* and the observed pressure and temperature be *P* and *T*.

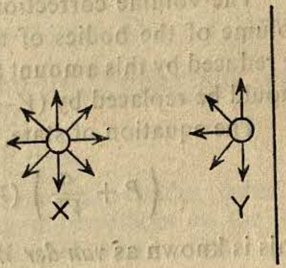


Fig. III.4a

The attractive force exerted on a single striking molecule would obviously depend upon the number of molecules present in the bulk, hence on density (*d*) of the gas. Again the number of molecules which would collide with the wall in unit time would also depend upon the density. Hence the total attractive force (p') which pulls the striking molecules backwards is proportional to the square of the density.

$$\therefore p' \propto d^2 \propto \frac{1}{V^2} \; ; \; \left(\text{since } d \propto \frac{1}{V}\right)$$

or $p' = a/V^2$, where a is a constant.

The quantity (a/V^2) is the additional amount of pressure (p') to be added to the observed pressure P. This is usually called the *internal pressure* or *cohesive pressure*. The ideal pressure should then be $\left(P + \frac{a}{V^2}\right)$.

Volume correction, v'. In deducing the ideal gas equation, the molecules were regarded as point-masses and hence the entire volume *V* was available for movement of each molecule. Since the molecules have definite size, the volume or space available for molecules to move about in real gases would be less. Assuming the molecules to be spherical, suppose r is the radius and $\sigma\,(=2r)$ be the diameter of a molecule of the gas, so that the volume of the body of each molecule, $b_1 = \frac{4}{3}\pi r^3 = \frac{1}{6}\pi\sigma^3$

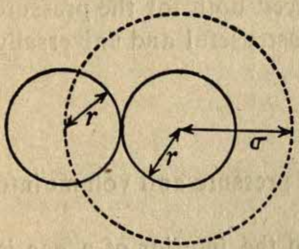


Fig. III.5. Excluded volume for a pair of molecules

When two molecules encounter each other, the distance between the centres of the two molecules would be σ. These cannot approach closer than this. This, in effect, takes into account the repulsive force between the molecules in close proximity. In consequence, as shown in the figure, a space indicated by the dashed circle having a diameter 2σ, will be unavailable to the pair of colliding molecules. This space, often called 'excluded volume' for the pair of molecules is $\frac{4}{3}\pi\sigma^3$, (Fig. III.5).

Then, the excluded volume for each molecule, $\beta' = \frac{2}{3}\pi\sigma^3$.

$$= 4 \times \frac{1}{6}\pi\sigma^3 = 4b_1$$

For a mole of the gas, such excluded volume will be, $4N_0b_1 = b$ (say), which is a constant.

The volume correction v' is thus b, which is equal to four times the actual volume of the bodies of the molecules. The observed volume should therefore be reduced by this amount (b) in computing the pressure of the gas. The volume V should be replaced by $(V-b)$.

The equation of state, corrected for the two factors, takes the form,

$$\left(P + \frac{a}{V^2}\right)(V-b) = RT, \qquad \text{(for 1 mole)} \qquad \ldots \text{(III.3)}$$

This is known as *van der Waals equation*.

If n moles of gas be present in volume v, the volume of one gm-mole would be v/n. So, we have,

$$\left(P + \frac{a}{(v/n)^2}\right)\left(\frac{v}{n} - b\right) = RT$$

or

$$\left(P + \frac{n^2a}{v^2}\right)(v-nb) = nRT, \quad \text{(for } n \text{ moles of a gas)} \quad \ldots \text{(III.4)}$$

'*a*' and '*b*' are called *van der Waals constants*; these are different for different gases. '*a*' is expressed in atm-litre^2-mole^{-2} and '*b*' in litre-mole^{-1}. The values of *a* and *b* of some gases are given here.

Table: van der Waals constants [*a* in litre^2-atm mole^{-2}, *b* in litre-mole^{-1}]

Gas	H_2	O_2	N_2	CO_2	NH_3	CH_4	*A*	*He*
a	0.244	1.36	1.39	3.59	4.17	2.25	1.35	0.034
b	0.027	0.032	0.039	0.043	0.037	0.043	0.032	0.024

Higher values of 'a' indicate stronger intermolecular attraction. Easily condensable gases have high values for 'a'. And 'b', which is often called 'co-volume', is a measure of the size of the molecules.

Notes: (*i*) At extremely low pressures and very high temperatures, the volume will be very large, so that the terms (a/V^2) and b are relatively very small. So that, the van der Waals equation may be approximated as,

$$\left(P+\frac{a}{V^2}\right)(V-b) = RT; \text{ or } PV = RT$$

i.e. under such conditions, real gases would behave ideally.

(*ii*) van der Waals eqn.: $\left(P+\frac{a}{V^2}\right)(V-b) = RT$

or
$$PV-Pb+\frac{a}{V}-\frac{ab}{V^2} = RT \qquad \ldots \text{(III.5)}$$

(*a*) At low pressures, P is small but V is large. The terms Pb and (ab/V^2) become quite small. So, approximately,

$$PV = RT-\frac{a}{V} = P_0V_0-\frac{a}{V}; \text{ (where } P_0V_0 \text{ is the value for ideal gases)}$$

Hence PV would be less than the ideal value at low pressures. This is evident in Amagat's isotherms (Fig. III.2):

(*b*) At high pressures, the last two terms in eqn (III.5) practically cancel one another being of opposite sign. So, approximately,

$$PV = RT+Pb = P_0V_0+Pb$$

This shows that at high pressures, PV-value would be larger than its ideal value.

(iii) van der Waals equation is certainly a great improvement on the ideal gas equation, yet it does not give the exactly accurate behaviour of gases. The following data would illustrate this.

TABLE A (Temp. 100°C)

Gas	Pressure observed	Pressure calculated from			
		ideal eqn	deviation	van der Walls	deviation
H_2	75	72.3	− 3.6%	75.7	+ 0.9%
	100	95.0	− 5.0%	100.8	+ 0.8%
CO_2	75	92.3	+ 17.3%	73.2	− 2.3%
	100	133.5	+ 33.5%	95.8	− 4.2%

Problem: At 27°C a 5-litre vessel contained two moles of ammonia. Calculate its pressure as (*i*) an ideal gas and as (*ii*) a van der Waals gas. Given $a = 4.0$ litre²-atm/mole², $b = 0.36$ litre/mole.

(*i*) As an ideal gas, $P = \frac{nRT}{v} = \frac{2\times 0.082\times 300}{5} = 9.84$ atm (*ii*) As a van der Waals gas, ($a = 4.0, b = 0.036$),

$$P = \frac{nRT}{v-nb} - \frac{an^2}{v^2}; \qquad \text{(eqn. III.4)}$$

$$= \frac{2 \times 0.082 \times 300}{5-2 \times 0.036} - \frac{4 \times 2^2}{5^2} = 9.34 \text{ atm}$$

3.5. Other Equations of State

Dozens of equations of state ($P-V-T$) have been proposed from time to time, all of them primarily attempting to correct the same two factors of van der Waals equation, namely, molecular interaction and the space used up by the molecules. Only a few of such equations are mentioned here.

(*i*) Dieterici: $P(V-b) = RTe^{-a/RTV}$

(*ii*) Berthelot: $\left(P + \frac{a}{TV^2}\right)(V-b) = RT$

(*iii*) Clausius: $\left(P + \frac{a}{T(V+C)^2}\right)(V-b) = RT$

(*iv*) Kammerling-Onnes: $PV = RT\left[1 + \frac{B}{V} + \frac{C}{V^2} + \ldots\right]$

The last equation is also called the *virial equation*, in which $B, C, D, \ldots$ are the second, third, fourth . . . virial coefficients.

3.6. Compressibility Factor

Real gases do not obey the kinetic gas equation, *i.e.* for real gases, $Pv \neq nRT$. Let us assume that, for real gases,

$$Pv = z.nRT \qquad \ldots \text{(III)}$$

where z is a factor which accounts for and covers the departure of real gases from ideal behaviour. 'z' is called the *compressibility factor*.

Since deviations for non-ideality are different in different circumstances, z will vary with the conditions of the system. For a clear idea of the extent or degree of non-ideality, z is plotted against P at different temperatures. Such $z-P$ isotherms for nitrogen are shown in Fig. III.6. The $z-P$ isotherms of other gases have all been found to be of the same form, though the individual values differ.

For an ideal gas at all pressures and temperatures, $Pv = nRT$ hence, $z = 1$. The $z-P$ isotherms of all gases tend to unit value of z at extremely low pressures, $\mathrm{Lt}_{p\to 0}$. Hence all gases tend to behave ideally at very low pressures.

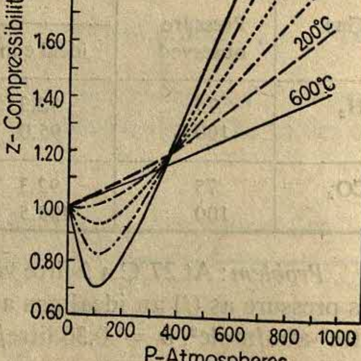


Fig. III.6. Compressibility factors for nitrogen

When $Pv < nRT$, z is less than 1.0, hence $z-P$ curve slopes downward at low ranges of pressure, showing the gas is more compressible than theoretically expected.

When $Pv > nRT$, z is greater than 1.0, indicating that the gas is less compressible than ideal gases. This is found in higher ranges of pressure.

The curves also indicate that z depends both on pressure and temperature.

Boyle Temperature : In Fig. III.7 are plotted the $PV-P$ isothermals of carbon dioxide, which are typical of other gases too. It is seen that with rise in temperature, the extent of higher compressibility decreases. As the temperature increases, the dips of the curves become shallower and flattened. The minimal points lie on a parabola and at relatively higher temperatures, the minimal points approach the PV-axis.

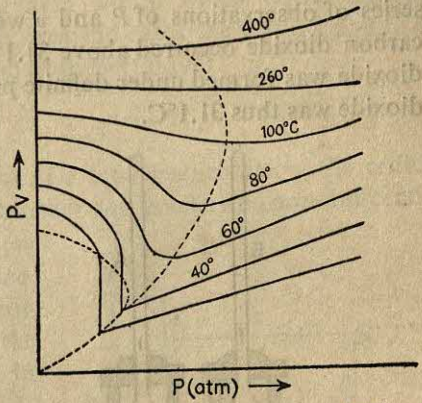


Fig. III.7. *PV-P* isotherms of CO_2

There exists for every gas a characteristic temperature, where the $PV-P$ curve runs sensibly parallel to the P-axis from zero pressure to moderate pressures. It means that at this temperature, PV remains constant for an appreciable range of pressure, *i.e.*, Boyle's law is obeyed. This temperature is known as the *Boyle temperature* (T_B) of the gas. If the plots of z vs P be observed (Fig. III.6), it is found that at about 59°C for nitrogen, z remains close to unity from $P=0$ atm to $P = 80$ atm. This temperatrure at which the real gas follows ideal gas law is the Boyle temperature of nitrogen.

At the Boyle temp. $$\underset{Lt\,P\to 0}{\left[\frac{\partial(PV)}{\partial P}\right]_T}=0$$

3.7. Critical State

Gases are liquefied by lowering the temperature and increasing the pressure. As temperature is lowered the kinetic energy of the molecules decreases, the slow-moving molecules come closer and they condense due to attraction. The increase of pressure has also the same effect. The influence of temperature is however more important. For every gas there is a temperature above which liquefaction is impossible whatever the pressure may be.

The limiting temperature above which liquefaction of a gas is impossible is called its *critical temperature* (T_c). Above the critical temperature the liquid state of the gas cannot exist.

The *critical pressure* (P_c) is the minimum pressure required to liquefy the gas at the critical temperature, T_c.

The volume occupied by a mole of the substance at the critical temperature and critical pressure is called its *critical volume* (V_c).

The idea of the critical state may be best explained from the classical experiments of Andrews (1869) on his investigations with carbon dioxide. He studied the *P-v* relations of this gas at different constant temperatures. An outline of Andrew's apparatus is given in Fig. III.8. In a narrow glass tube *A*, a small quantity of CO_2-gas was enclosed and sealed by a pellet of mercury. This glass tube was fitted into a strong copper tube *X* entirely filled with water. An exactly similar arrangement was made in the other half of the apparatus, where in a similar narrow tube *B* a known quantity of air was enclosed. By measuring the volume of this air, the pressure was known, which was also the pressure of CO_2. The pressure could be increased up to about 400 atm by pushing screws at the bottom of the water cylinders. The carbon-dioxide tube was kept surrounded by jackets maintained at suitable temperatures. At each temperature, a series of observations of *P* and *v* were made. He found that no liquefaction of carbon dioxide occurred above 31.1°C. Below this temperature, liquid carbon dioxide was formed under definite pressures. The critical temperature of carbon dioxide was thus 31.1°C.

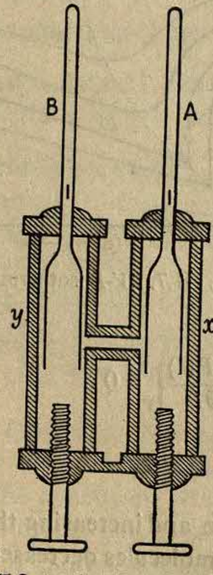


Fig. III.8. Andrew's apparatus

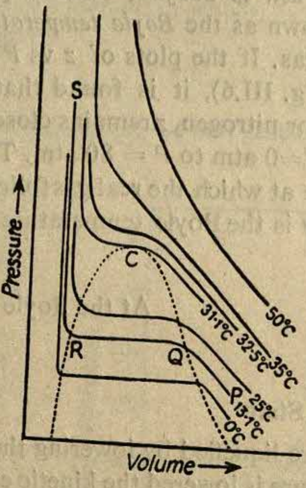


Fig. III.9. *P–v* curves for carbon dioxide

The isothermals obtained by plotting the observed *P-v* data of Andrew's experiments are shown in Fig. III.9. From Boyle's Law, these curves are expected to be rectangular hyperbola. At higher temperatures, say 50°C, the isotherms look similar to those for ideal gases. But as the temperature is lowered the isotherms deviate increasingly from the theoretically expected curves. At low temperatures, say 13.1°C, the isotherm *PQRS* consists of three parts. The volume of the gas at *P* decreases along *PQ* with increase in pressure. Then there is a horizontal portion *QR* showing considerable decrease in volume with practically no change in pressure, indicating the process of liquefaction, When liquefaction is complete at *R*, the isotherm rises steeply, because volume-decrease is very small even for large increase in pressure. At other low temperatures, similar isotherms are obtained, but the horizontal portion gradually decreases with increase in temperature. At 31.1°C, the horizontal portion of the isotherm virtually reduces to a mere point C. Above this temperature, there is no horizontal section and liquefaction does not take place. The isotherm at 31.1°C is the critical isotherm and this temperature is the critical temperature. The point C denote the *critical state* of the substance, as it is then at critical temperature and under critical pressure. At the critical state, the liquid and gaseous states are indistinguishable. Generally, the substances in the gaseous phase below the critical temperature are called *vapours* and the term, *gases*, is generally used when the temperature is above the critical temperature.

The dotted line indicates a dome-shaped area within which liquid and gas are co-existent. The highest point C of the area indicates the critical point. At the right of this area gas alone is present and at the left liquid.

3.8. Continuity of State

An examination of the *P-v* isothermal at a temperature below the critical temperature may lead one to believe that since there are breaks and non-uniformity in the curve, the transformation of the gas into liquid would be a discontinuous one. But this is not so. Consider the isotherm *ABCD* at T° ($< T_c$). It is obvious that the substance is in the gaseous state at *P* and in the liquid state at *S* (Fig. III.10).

Suppose the gas at *P* is raised in temperature at constant volume along *PQ*. From the point *Q*, the gas is gradually cooled at constant pressure along *QR*. The volume will be reduced considerably. On reaching *R*, the gas is again cooled at constant volume until the point *S* is reached. Nowhere in this process would liquid appear. At *S*, the system is a highly compressed gas. But we know from the isotherm that the system is in liquid state at the point *S*. Hence there is hardly any distinction between the liquid and the gaseous state. There is no line of demarcation or abrupt change between the two phases. This is known as the *continuity of state*. The transition of one state into another is practically imperceptible.

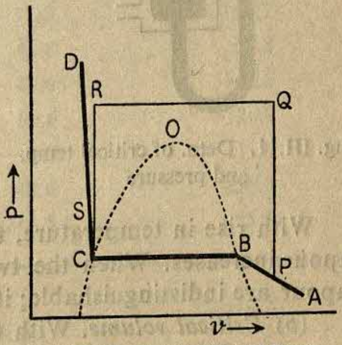


Fig. III.10. Continuity of State

3.9. Determination of Critical Constants

(*a*) *Critical pressure and temperature*. The critical temperature as well as pressure can be simultaneously measured with an apparatus as shown in Fig. III.11. A small quantity of the substance is enclosed over mercury in a closed bulb A. This is attached to a manometer B in which a known amount of air is kept over mercury. The bulb A is surrounded by a jacket, the temperature of which can be adjusted according to requirements. Initially, the temperature is maintained at such a level that the substance remains partly as liquid and partly as vapour. The surface of separation between the liquid and the vapour is carefully observed. The temperature is then very slowly raised until the meniscus just disappears. On slightly lowering the temperature, the surface would reappear. The temperature at which the surface disappears is noted and it is the critical temperature. Simultaneously the critical pressure is recorded from the manometer.

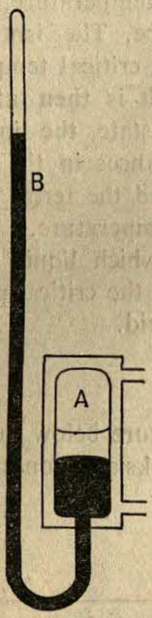


Fig. III.11. Detn. of critical temp. and pressure

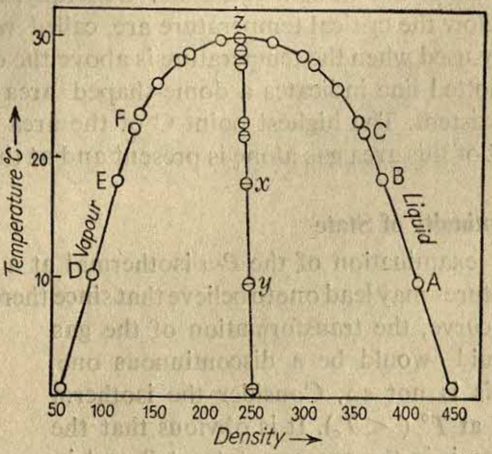


Fig. III.12. Density of saturated vapour and liquid CO_2 (densities are given in Amagat units)

With rise in temperature, the density of liquid decreases and that of satd. vapour increases. When the two densities become equal, the liquid and the vapour are indistinguishable; it is the critical state.

(*b*) *Critical volume*. With the rise in temperature, the density of a liquid decreases while the density of its saturated vapour increases. If these densities of liquid and *saturated* vopour be plotted against temperature, curves *ABC* and *DEF* are obtained as in Fig. III.12. It was discovered by Cailletet and Mathias that the mean of the densities of liquid and saturated vapour bears a linear relation to temperature. That is, when the mean of the points on *ABC* and *DEF* are plotted, a straight line *xy* is obtained. This is commonly called the *law of Cailletet and Mathias*. If d_l and d_g denote the two densities, then

$$\tfrac{1}{2}(d_l + d_g) = a + bt \qquad \ldots \text{(III. 6)}$$

where a and b are constants.

This is also known as the *law of Rectilinear diameters*.

The two curves *ABC* and *DEF* are extrapolated to cut at *z*, where the densities of the saturated vapour and the liquid are equal. This would occur only at the critical temperature. The point *z* corresponds to the critical density (d_c) and it would obviously be on the mean-density line *xy*. Hence, the critical volume would be M/d_c.

The critical constants of some common substances are given here.

CRITICAL CONSTANTS

Gas	*Critical temperature* °K	*Critical pressure* (*atm.*)	*Critical volume* (*c.c.*)
Oxygen	154.28	49.7	74.4
Hydrogen	33.2	12.8	69.7
Nitrogen	125.97	33.5	90.0
Ammonia	405.5	111.3	72.0
Carbon monoxide	133.0	34.5	90.0
Carbon dioxide	304.15	72.9	94.2
Chlorine	417.0	76.1	123.5
Sulphur dioxide	430.25	77.7	125.0
Helium	5.2	2.25	61.55
Neon	44.75	26.86	44.30
Argon	150.6	77.0	150.7
Methane	190.3	45.6	98.8
Ethane	305.4	48.0	142.8
Ethylene	283.0	50.6	126.0
Acetylene	308.6	61.7	113.0
Benzene	562.0	48.6	256.0
Water	647.3	218.5	55.54

3.10. van der Waals Equation and critical phenomenon

With the knowledge of '*a*' and '*b*', the volumes of a real gas at different pressures can be evaluated at a given temperature from van der Waals equation. With these values, van der Waals equation can be graphically represented by a *P-v* isotherm. Such theoretical *P-v* isotherms of van der Waals equation for CO_2 gas at different temperatures are given by solid lines in Fig. III.13. The experimentally observed *P-v* isotherms or Andrews curves are given in dotted lines. It will be noticed that at higher temperatures, the two curves are more or less the same.

But at lower temperatures, there is considerable divergence between the theoretical and experimental curves, especially in the region where liquid and gas coexist. In this region, experimental curves are horizontal whereas the theoretical curves are ~ shaped with a minimum and a maximum. With increase in temperature, we have seen that the horizontal portions of Andrews curves gradually diminish and ultimately coalesce into a point C at the critical temperature. In the theoretical curves also, the minimum and the maximum points approach each other and then reduce to a point in the critical temperature isotherm.

The van der Waals equation,

$$\left(P + \frac{a}{V^2}\right)(V-b) = RT$$

may be written, after multiplying and rearranging, as

$$V^3 - \left(b + \frac{RT}{P}\right)V^2 + \frac{a}{P}V - \frac{ab}{P} = 0$$

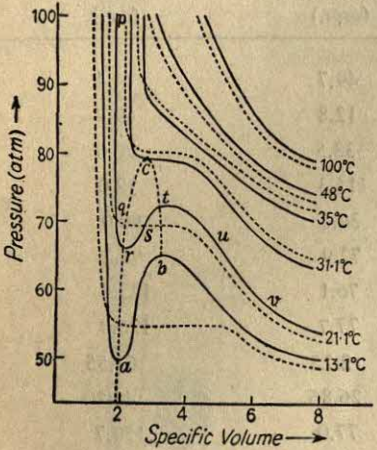


Fig III.13. P-V isothermals of CO_2 (Dotted lines experimental ; bold lines theoretical)

It is a cubic equation in V and it may have three roots. All the roots may be real or one real and two imaginary. If a curve below critical temperature be observed, say the isotherm at 21.1°C in Fig. III.13, for a pressure of about 70 atm, the volume may have three values as given by q, s and u. But at the critical isotherm, the three roots would merge into one and would be the critical volume, V_c.

At the critical point, the van der Waals equation is

$$V^3 - \left(b + \frac{RT_c}{P_c}\right)V^2 + \frac{a}{P_c}V - \frac{ab}{P_c} = 0 \qquad \ldots \text{(A)}$$

Since the roots are all equal to V_c, we have

$$(V - V_c)^3 = 0;$$

or

$$V^3 - 3V_cV^2 + 3V_c^2V - V_c^3 = 0 \qquad \ldots \text{(B)}$$

Equating the coefficients of equations (A) and (B),

$$(i)\ 3V_c = b + \frac{RT_c}{P_c} \qquad (ii)\ 3V_c^2 = \frac{a}{P_c} \qquad (iii)\ V_c^3 = \frac{ab}{P_c}$$

Dividing (ii) by (iii); $V_c = 3b$

Substituting V_c in (ii); $P_c = \dfrac{a}{27b^2}$

Putting the values of P_c and V_c in (i),

$$3 \times 3b = b + \frac{RT_c}{a/27b^2}\ ; \ i.e.\ T_c = \frac{8a}{27Rb}$$

Hence critical constants can be expressed in terms of van der Waals constants;

$$V_c = 3b, \ P_c = a/27b^2, \ T_c = 8a/27Rb \qquad \ldots \text{(III.7)}$$

$$\therefore \quad \frac{RT_c}{P_cV_c} = R \times \frac{8a}{27Rb} \times \frac{27b^2}{a} \times \frac{1}{3b} = \frac{8}{3} \qquad \ldots \text{(III.8)}$$

That is, the critical coefficient (RT_c/P_cV_c) of a van der Waals gas should have a constant value of 2.67.

But for most of the gases, the RT_c/P_cV_c value is almost constant but it is not 2.67. Often the values are above 3.0.

Again, the van der Waals constants may be expressed as,

$$a = \frac{27R^2T_c^2}{64P_c} \quad \text{and} \quad b = \frac{RT_c}{8P_c} \qquad \ldots \text{(III.9)}$$

$$\text{Also} \qquad a = 3P_cV_c^2 \quad \text{and} \quad b = \tfrac{1}{3}V_c$$

This shows that though van der Waals equation deals with the situation in real gases in the proper direction, it is inadequate in its quantitative aspect.

3.11. The Law of Corresponding States

Since the critical constants are definite quantities for a gas, it is possible to express its, P, V, T, the pressure, volume and temperature in any given state as multiples or sub-multiples of the critical values, Let us say,

$$P = \pi P_c, \quad V = \phi V_c \quad \text{and} \quad T = \theta T_c$$

where π, ϕ and θ which are numbers called reduced pressure, reduced volume and reduced temperature. These numbers indicate how many times the critical values are greater or smaller than the respective given quantities.

The van der Waals' equation may then be changed as.

$$\left(P + \frac{a}{V^2}\right) (V-b) = RT$$

$$\text{or} \qquad \left(\pi P_c + \frac{a}{\phi^2 V_c^2}\right) (\phi V_c - b) = R\theta T_c$$

Substituting the critical constants by equation (III.7)

$$\left(\frac{\pi a}{27b^2} + \frac{a}{9\phi^2 b^2}\right) (3\phi b - b) = R\theta \frac{a}{27bR}$$

$$\text{or} \qquad \left(\pi + \frac{3}{\phi^2}\right) (3\phi - 1) = 8\theta$$

This relation in terms of the reduced parameters of the system is called the van der Waals *reduced equation of state.* The most interesting aspect of this relation is that it would be applicable to all gases, since it is independent of the constants a, b and R.

The equation implies that *if two substances have the same reduced pressure* π *(i.e., their pressures are* π *times their respective critical pressures) and are also at the same reduced temperature* θ, *(i.e., their temperatures are* θ *times their respective critical temperatures), then their reduced volumes* ϕ *should be the same, (i.e., the ratio* $\frac{V}{V_c}$ *should be the same).* Substances under such conditions are said to be in corresponding states and the principle is the **Law of corresponding states.**

3.12. Calculations

Problem: For water, the critical constants are $P_c = 218$ atm, $T_c = 647$°K, $V_c = 0.057$ litre/mole. Calculate van der Waals constants.

$$a = 3P_cV_c^2 = 3 \times 218 \times (0.057)^2 = 2.10 \text{ litre}^2 \text{ atm/mole}^2$$
$$b = V_c/3 = 0.057/3 = 0.019 \text{ litre/mole.}$$

Problem: The van der Waals constant b of a gas is 0.027 litre/mole. Calculate the radius of its molecules.

Suppose r is the radius of a molecule. Then $b = 4N_0(\frac{4}{3}\pi r^3)$,
or $27(\text{c.c.}) = 4 \times 6.02 \times 10^{23} \times \frac{4}{3} \times 3.14 \times r^3$
when $r = 2.68 \times 10^{-8}$ cm

Problems: Calculate van der Waals' constants for ethylene. ($T_c = 282.8$°K and $P_c = 50$ atm.)

$$b = \frac{1}{8}\frac{RT_c}{P_c} = \frac{1}{8} \times \frac{0.082 \times 282.8}{50} = 0.057 \text{ litres/mole}$$

$$a = \frac{27}{64}R^2 \cdot \frac{T_c^2}{P_c} = \frac{27}{64} \times (0.082)^2 \times (282.8)^2 \times \frac{1}{50}$$
$$= 4.47 \text{ litres}^2\text{-atmospheres/mole}^2$$

Problem: 100 gm of CO_2 are contained in a 5-litre globe at 40°C. Calculate its pressure (*i*) as a van der Waals' gas, (*ii*) as an ideal gas. ($a=3.59$, $b=0.043$)

$$\text{Ideal}: \quad P = \frac{nRT}{v} = \frac{100}{44 \times 5} \times 0.082 \times 313 = 11.67 \text{ atm.}$$

$$\text{van der Waals'}: P = \frac{nRT}{v - nb} - \frac{n^2a}{v^2}$$

$$= \frac{100 \times 0.082 \times 313}{44\left(5 - \frac{100}{44} \times 0.043\right)} - \frac{\left(\frac{100}{44}\right)^2 \times 3.59}{25}$$

$$= 11.16 \text{ atm.}$$

Problem: Argon has ($T_c = -122$°C, $P_c = 48$ atm). What is the radius of the Argon atom?

$$b = \frac{1}{8}\frac{RT_c}{P_c} = \frac{1}{8} \times \frac{0.082 \times 151}{48}$$

$$\therefore \; 4 \times \frac{4}{3}\pi r^3 \times N_0 = b = \frac{1}{8} \times \frac{0.082 \times 151}{48} \text{ litre}$$

$$r = \left[\frac{0.082 \times 151 \times 3 \times 10^3}{8 \times 48 \times 16 \times 3.14 \times 6 \times 10^{23}}\right]^{\frac{1}{3}} \text{ cm}$$

$$= 1.47 \times 10^{-8} \text{ cm}$$

Problem: One litre of a gas at 300 atm and 473°K is compressed to a pressure of 600 atmosphere and 273°K. The compressibility factors found from the curves are 1.072 and 1.375 respectively at the initial and final states. Calculate the final volume.

$$P_1v_1 = z_1nRT_1 \qquad P_2v_2 = z_2nRT_2$$

$$\text{or} \quad \frac{P_2v_2}{T_2} \cdot \frac{T_1}{P_1v_1} = \frac{z_2}{z_1} \qquad (\text{where } v_2 = \text{final volume})$$

$$\text{or} \quad v_2 = \frac{z_2}{z_1} \cdot \frac{T_2}{T_1} \cdot \frac{P_1v_1}{P_2} = \frac{1.375}{1.072} \times \frac{273}{473} \times \frac{300 \times 1}{600} = 370.1 \text{ c.c.}$$

EXERCISES

I

1. Give a brief account of the deviations observed with gases from the perfect gas equation. How are these accounted for?

2. Deduce van der Waals equation and clearly explain the constants in the equation. In what units are these constants expressed?

3. Discuss van der Waals equation for real gases. Give the relations between van der Waals constants and the critical constants.

4. Give a concise account of the arguments which led to the formulation of van der Waals equation. State the equation and show how a and b are related to critical constants.

5. Define the critical constants of a gas. How would you proceed to determine the constants?

6. What is the law of corresponding states. Deduce the reduced equation of state for van der Waals gases.

7. Write brief notes on: (*i*) Continuity of state (*ii*) Reduced equation of state (*iii*) Boyle temperature (*iv*) principle of Cailletet & Mathias.

8. What is an ideal gas? What facts are revealed from Amagat's Pv–P isotherms? What is compressibility factor and how does it explain the nature of non-ideality of a gas?

9. Suggest a method for determining the van der Waals constants.

10. Two van der Waals gases have the same a–values but b–values are different; which one would be more compressible?

11. Justify or correct: (*i*) "The b–value of a gas is found to be negligible, hence its critical volume will be almost nil."

(*ii*) "Two moles of CO_2 (van der Waals gas) are enclosed in a vessel and its pressure is P. Another two moles of the gas at the same temperature are introduced into it. The pressure should be $2P$."

(*iii*) At low pressure and high temperature, a real gas tends to behave ideally.

(*iv*) "At low pressure and temperature, a gas, say CO_2, would be less compressible than an ideal one."

II

12. Find the temperature at which 3 moles of SO_2 will occupy a volume of ten litres at 15 atm, using van der Waals equation. [$a = 6.71$, $b = 0.056$, in atm-litre units] [Ans. 350°C]

13. Ten gm ammonia are contained in a litre-flask at 0°C. Calculate the pressure if it behaves as a van der Waals gas. [$a = 4.17$ atm litre^2/mole^2, $b = 37.1$ c.c.] [Ans. 12.02 atm]

14. A mole of water vapour at 150°C is contained in a 10-litre vessel. Estimate its pressure (*i*) as an ideal gas and (*ii*) as a van der Waals gas. [$a = 5.464$ liter^2-atm-mole^{-2} and $b = 0.0305$ litre-mole^{-1}] [Ans. 3.47; 3.43 atm]

15. At 48°C, one mole of CO_2 occupied a volume of 1.32 litres. What would be its pressure if it behaves as (*i*) an ideal gas and (*ii*) a van der Waals gas. Given $b = 0.043$ liter mole^{-1} and $a = 3.6$ atm liter^2 mole^{-2}]. [Ans. 19.9; 18.5 atm]

16. Van der Waals constants in litre-atmosphere units are $a = 3.6$, $b = 4.28 \times 10^{-2}$. Calculate the critical temperature and critical volume of the gas. (Poona Univ.) [Ans. 31°C; 12.8 × 10^{-2} litres]

17. Calculate van der Waals 'a' and 'b', if P_c and T_c of the gas be 72.8 atm and 31°C respectively. (Bombay Univ.) [Ans. 3.6; 4.3]

18. Calculate van der Waals constants for oxygen, when $P_c = 49.7$ atm and $T_c = 154.2°K$. (Calcutta Univ.) [Ans. $a = 1.36$ atm-litre^2-mole^{-2}; $b = 0.032$ litre/mole]

19. Van der Waals constants for nitrogen are $a = 1.39$, $b = 3.9 \times 10^{-2}$ in atmosphere-litre units. Find out its critical constants. (Calcutta Univ.)
[Ans. $P_c = 33.67$ atm, $T_c = -144.7°C$, $V_c = 11.73 \times 10^{-2}$ litre]

20. The co-volume 'b' of a gas is 4.42×10^{-2} litre mole^{-1}. Find out the diameter of its molecules. (Calcutta Univ.) [Ans. 3.273×10^{-8} cm]

21. Calculate the wt. of O_2 necessary to fill up a cylinder of 5 litre capacity at 0°C and 100 atm when the compressibility factor is 0.96. [Ans. 744.4 gm]

22. At 323°K, 1 mole of a gas occupies a volume of $4 \times 10^{-4} m^3$ under a pressure of 5.152×10^6 Nm^{-2}. Calculate the value of 'a' using van der Waals eqn., if $b = 4.27 \times 10^{-5}$ m^3/mole. [Ans. 0.38 Nm^4K mol^{-2}]

CHAPTER 4

MOLECULAR WEIGHTS OF GASES

4.1. Absolute density and Vapour density

The absolute density (d) of a gas or vapour is its mass per unit-volume; $d = M/v$. This is mentioned simply as density. It is related to the molecular weight by the kinetic gas equation (I.10):

$$Pv = \frac{g}{M}RT \qquad \text{or} \qquad M = d\frac{RT}{P}$$

Using c.g.s. units, 'd' in this equation would be in gm/c.c.

Vapour-density: The density of a gas relative to the density of hydrogen at the same temperature and pressure is called its 'Vapour density' (D) or 'Relative density'.

$$D = \frac{d_{\mathbf{gas}}}{d_{\mathbf{H_2}}} = \frac{M_{\mathbf{gas}}}{M_{\mathbf{H_2}}}$$

$$\text{or} \quad M_{\mathbf{gas}} = D \times M_{\mathbf{H_2}} = 2.016 \times D \qquad \ldots \text{(IV.1)}$$

The vapour density is thus a pure number.

Very often densities are used to determine the molecular weights of gases.

4.2. Methods for Determination of Molecular weights

There are a number of methods for the determination of molecular weights of gases. Some of these are mentioned here briefly.

I. Regnault's method: It is one of the oldest methods to determine the density of a gas. A large glass globe of capacity of 500 c.c. ~ 1000 c.c., fitted with a stop-cock is first very carefully dried and then evacuated and weighed. It is then filled with the gas under investigation at a known temperature and pressure. It is weighed again. During the weighing the globe is always counterpoised by an exactly similar evacuated globe hung in the other arm of the balance. The difference of the two weights—evacuated and gas-filled—of the bulbs, gives the weight of the gas (g). The volume of the globe (v) is known by weighing the globe filled up with water (or mercury) whose density is known. Hence density $d = g/v$ is known.

Using the relation, $M = d.RT/P$, the molecular weight would be easily obtained.

II. Buoyancy Microbalance Method : From the beginning of this century, buoyancy microbalance has been used for the determination of gas density wherever high degree of accuracy is required and specially when the quantity of the gas is small.

The microbalance used by Whytlaw-Gray in the determination of the density of radon (Fig. IV.1) consisted of an evacuated quartz buoyancy globe X, (8 c.c.)

suspended at one end of a quartz beam Z. This was counterbalanced by a thin sheet of quartz Y, at the other end of the beam, the surface areas of the globe and the sheet being almost equal. The beam was suspended from a frame by a stretched quartz fibre T. The whole thing was enclosed inside a container of about 10 cm length kept at a constant temperature (say 0°C) and provided with a manometer. The container is first evacuated and the gas is then slowly introduced until a pointer at the end of Y points to a fixed zero mark O. The pressure P_1 is noted. The experiment is then repeated with pure oxygen gas and the corresponding pressure P_2 is also determined.

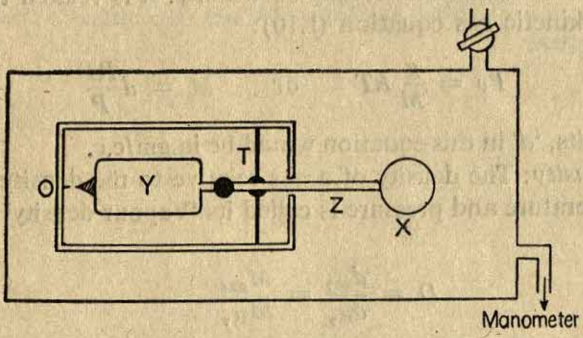


Fig. IV.1. Buoyancy microbalance.

It is easily seen that whenever the globe would counterbalance the quartz sheet, the density of the gas introduced must be the same.

If v_1 and v_2 be the volumes of the globe and the sheet and w_1 and w_2 be their true weights respectively, then when these two exactly balance one another, we have

$$w_1 - v_1 d = w_2 - v_2 d$$

where d is the density of the gas.

$$\therefore d = (w_1 - w_2)/(v_1 - v_2)$$

Since w_1, w_2, v_1 and v_2 are all fixed, the density of the gas shall always be the same whenever they balance one another.

In this experiment, suppose ρ_1 be the density of the gas under pressure P_1 and ρ_2 be the density of the other under pressure P_2. Then,

$$\rho_1 = \rho_2$$

$$\text{But} \qquad \rho_1 = \frac{P_1 M_1}{RT} \qquad \text{and} \qquad \rho_2 = \frac{P_2 M_2}{RT}$$

$\therefore \rho_1 = P_2 M_2 / RT$; or the density of the gas is known. M_1, M_2 are the mol. wts of the gas and oxygen respectively.

$$\text{Further} \qquad P_1 M_1 = P_2 M_2, \text{ or } M_1 = (P_2/P_1) M_2 \qquad \ldots (I.20)$$

Hence the mol. wt. is also obtained directly.

Problem : At 0°C, the density of a gaseous non-metallic oxide at 2 atm. is the same as that of oxygen at 5 atm. Find the mol. wt. of the gas.

$$M = (P_2/P_1)M_2 = \frac{5}{2} \times 32 = 80$$

Density of vapours. Several methods used to determine the density of vapours (which are often employed in the laboratory) are described here.

III. Hofmann's Method: In this method a known weight of the liquid is introduced into the vacuum over mercury in a barometer at a temperature higher than the *b.pt.* of the liquid. The barometer is surrounded by a jacket through which the vapour of a high boiling liquid is passed to maintain the barometer at a sufficiently high and constant temperature. In Fig. IV.2 is given an outline of the arrangement. In a small Hofmann bottle a small quantity of liquid (of known weight) is introduced into the barometer tube. The bottle goes to the top of the mercury column and the liquid vaporizes depressing the mercury column. The volume of the vapour is directly read from the scale, the depression gives the pressure and the temperature is also noted. The normal vapour density may be easily obtained.

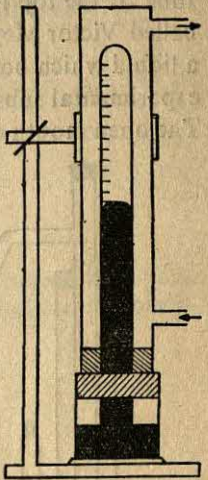


Fig. IV.2. Hofmann's apparatus for determination of vapour density

Let the weight of liquid vaporised = g gm
the volume of vapour measured = v c.c.
the initial height of mercury column = h_1 cm
the final height of mercury after vaporisation = h_2 cm
the temperature = T°K

$$\text{Then, } M = \frac{g}{v} \cdot \frac{RT}{(P_1 - P_2)} = \frac{g}{v} \times \frac{8.4 \times 10^7 \times T}{(h_1 - h_2) \times 13.6 \times 981}$$

Since the pressure of the vapour $P = P_1 - P_2 = (h_1 - h_2)\,dg$

Problem: In a Hofmann apparatus 0.2704 gm of a liquid was vaporised. The volume of the vapour was 113 c.c. at 100°C. The atmospheric pressure was 747 mm and the height of mercury in the tube was 285 mm. Find out its mol. wt.

$$M = \frac{gRT}{Pv}; \quad 113 \text{ c.c.} = 0.113 \text{ litre}, \quad 100°\text{C} = 373°\text{K}$$

$$R = 0.082 \text{ litre-atm}$$

$$P = (747 - 285) \text{ mm} = 462 \text{ mm} \equiv (462/760) \text{ atm.}$$

$$\text{Hence, } M = \frac{0.2704 \times 0.082 \times 373}{(462/760) \times 0.113} = 120.4$$

IV. Victor Meyer's Method. For its simplicity and convenience of operation, this method is most frequently used. The principle involved is that the vapour produced from a known weight of the liquid is allowed to displace an equal volume of air, which is collected and measured at room temperature and pressure.

One form of the apparatus is shown in Fig. IV.3. A long tube (about 1 cm diameter) ending in an elongated bulb at the bottom and having a capillary side tube at the top is used for vaporizing the liquid. This vaporization tube is often called Victor Meyer's tube. It is surrounded by a glass or copper jacket containing a liquid which boils at a temperature 20° or 25° higher than the boiling pt. of the experimental substance and maintains a constant temperature for the inner tube. The open mouth of the vaporization tube is closed by means of a rubber cork and the outer end of the side-tube is kept immersed in a trough of water. The liquid in the outer jacket is allowed to boil sufficiently long so that the steady condition is reached. This is indicated by the cessation of bubbles coming out through the capillary tube. A graduated measuring tube filled with water is now kept inverted over the end of the capillary tube.

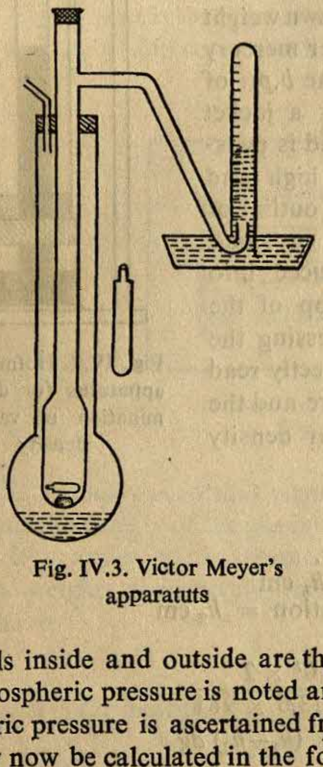


Fig. IV.3. Victor Meyer's apparatuts

A minute bulb or a small Hofmann bottle containing a known amount of the experimental liquid (about 0.15 gm), is then dropped into the vaporization tube by momentarily removing the rubber cork from its mouth. As soon as the bottle reaches the bottom of the Victor Meyer tube, the liquid vaporizes and pushes out an *equal volume of air* through the capillary side-tube to the graduated measuring tube. The graduated tube containing the collected air is then partly immersed in the same inverted manner into a tall jar of water such that water levels inside and outside are the same. The volume of the moist air under the atmospheric pressure is noted and also the temperature of the water. The atmospheric pressure is ascertained from the barometric reading. The vapour density may now be calculated in the following way:

Suppose Weight of the liquid taken $= g$ gm
Volume of the moist air collected $= v$ c.c.
Barometric height $= P$ mm
Temperature $= t$°C
Aqueous tension at t°C $= f$ mm

Let v_0 be the volume of the collected air at N.T.P. in dry state.

Then, $$\frac{v_0 \times 760}{273} = \frac{v \times (P-f)}{273+t} \quad \text{or} \quad v_0 = \frac{v(P-f)273}{(273+t)760}$$

Hence normal density, $$\rho_0 = \frac{g}{v_0} = \frac{g(273+t)760}{v(P-f)273} \text{ gm/c.c.}$$

These data are used in obtaining molecular weight. The calculation can be made in different ways.

(*i*) Since normal density is ρ_0, hence vapour-density $= \dfrac{\rho_0}{\rho_{H_2}}$

$$\therefore \text{ mol. wt., } M = 2.016 \times D = \frac{2.016 \times \rho_0}{\rho_{H_2}} = \frac{2.016 \times \rho_0}{0.00009} \text{ ; (eqn. IV.1)}$$

(*ii*) The mol. wt. can be evaluated by using the kinetic gas equation.

$$M = \frac{g}{v}\frac{RT}{P} = \frac{g}{v \times 10^{-3}} \times \frac{0.082 \times T}{(P-f)/760}$$

(*iii*) At N.T.P. v_0 c.c. is the volume of g gm

$$22400 \text{ c.c. is the volume of } \frac{g \times 22400}{v_0} \text{ gm}$$

Hence, by Avogadro's Law, the mol. wt. $M = (g \times 22400)/v_0$

Problem: In a Victor Meyer's experiment, 0.16 gm of a substance on vaporisation displaced 26.2 c.c. of moist air at 17°C and 764 mm pressure (aqueous tension at 17°C = 14 mm) Find M.

$$Pv = \frac{g}{M} \times RT$$

$$\frac{764-14}{760} \times \frac{26.2}{1000} = \frac{0.16}{M} \times 0.082 \times 290$$

$$\text{when } M = 147.1$$

Problem: 0.1743 gm carbon tetrachloride on vaporisation in Victor Meyer's apparatus displaced 26.7 ml. of air at 12°C and 759 mm. The aq. tension at 12°C is 11 mm. Calculate its molecular weight.

Let v_0 be the volume of displaced gas collected at N.T.P.

$$\text{So,} \quad \frac{v_0 \times 760}{273} = \frac{(759-11) \times 26.7}{285}$$

$$\text{or} \quad v_0 = \frac{748 \times 26.7 \times 273}{285 \times 760} \text{ c.c.}$$

$$\therefore \text{ normal density of the vapour} = \frac{0.1743 \times 285 \times 760}{748 \times 26.7 \times 273} \text{ gm/c.c.}$$

$$\therefore \text{ Vapour density} = \frac{0.1743 \times 285 \times 760}{748 \times 26.7 \times 273 \times 0.00009} = 77.0$$

$$\therefore \text{ Mol. wt. of carbon tetrachloride} = 2.016 \times 77 = 155.2$$

V. Duma's Methods: A dry retort-like glass globe with a narrow elongated neck ending into a capillary (Fig. IV.4) is taken and weighed. Its volume is predetermined. It is then heated with its narrow neck dipped into the liquid whose density is to be found out. On cooling, some liquid will enter into the globe. The globe is then placed in a hot bath whose temperature (T_1°K) is at least 20°C higher than the boiling pt. of the liquid taken inside. After sometime when the liquid inside has completely vaporised and steady state is reached, the tip of the capillary is sealed with a jet-flame, The globe containing the vapour now, is cooled and

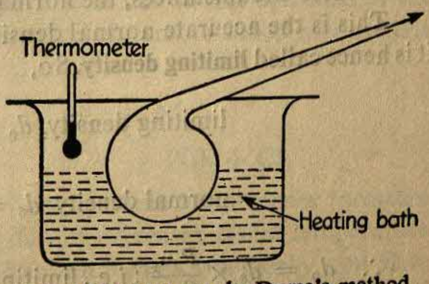


Fig. IV.4. Mol. wt. by Duma's method

weighed again. All weights are taken at room temperature (T°K). The barometric height (B) is also noted.

Suppose wt. of the globe with air $= w_1$ gm
wt. of the globe with vapour $= w_2$ gm
the volume of the globe $= v$ c.c.

Now v c.c. air is present in the globe. At N.T.P. its volume,

$$v_0 = \frac{v \times B}{T} \times \frac{273}{760}$$

Again v c.c. vapour is present in the globe at T_1°K and B mm pressure, hence at N.T.P., its volume

$$v_0' = \frac{v \times B}{T_1} \times \frac{273}{760}$$

The density of air $= 0.00129$ gm/cc.
The wt. of air filling the globe, $w_a = v_0 \times 0.00129$ gm
wt. of the globe only $= w_1 - w_a$
wt. of the vapour filling the globe $= w_2-(w_1-w_a) = w_2-w_1+w_a$
$\therefore$ At N.T.P., v_0' c.c. vapour weights $(w_2-w_1+w_a)$ gm

or 22400 c.c. vapour weighs $\dfrac{(w_2-w_1+w_a) \times 22400}{v_0'}$ gm

which is the mol. wt. of the vapour.

VI. From rate of diffusions: We have already seen in Sec (I.8.) how by measuring the rate of diffusion of a gas relative to that of a known gas the mol. wt. can be determined, using Graham's Law.

4.3. Limiting density

In measuring the densities of gases and vapours, in the previous section, the ideal gas equation was used. This equation is not valid for real gases, hence adequate corrections for the measured densities are required.

Suppose w gm of a gas or vapour has a volume v_1 at a pressure P_1. Then its density under pressure P_1 is w/v_1. The temperature is kept constant, say at 0°C. Then, the density under unit pressure, or the normal density, $d_s = \dfrac{w}{P_1 v_1}$.

But $P_1 v_1$ is not constant; the normal density will thus vary with the pressure at which the measurement is made. An accurate value of the normal density can be obtained only if measurements are made at extremely low pressure, $P_{0,\ Lt P \to 0}$, where the gases behave ideally. Let v_0 be the volume of the gas under pressure P_0. Under these circumstances, the normal density would be $w/P_0 v_0$

This is the accurate normal density d_0 obtained under limiting values of PV. It is hence called **limiting density.** So,

$$\text{limiting density, } d_0 = \frac{w}{P_0 v_0}$$

$$\text{normal density } d_s = \frac{w}{P_1 v_1}$$

$\therefore\ d_0 = d_s \times \dfrac{P_1 v_1}{P_0 v_0}$; *i.e.*, limiting density = normal density $\times \dfrac{P_1 V_1}{P_0 v_0}$

There are several methods for computation of limiting density. One method is mentioned here.

If *d* be the density of a gas or vapour under pressure *P*(temperature constant), then the normal density is *d*/*p*. It has been found that at low pressures (below 1 atm), *d*/*P* decreases practically linearly with pressure *P* (Fig. IV.5). Extrapolation of this line to zero pressure gives the ideal value of $(d/p)_{Lt\,P\to 0}$. This is hence the *limiting density* of the gas or vapour.

From the ideal gas equation

$$M = \frac{dRT}{P} = \left(\frac{d}{P}\right)_{P\to 0} RT$$

Thus from a knowledge of limiting density, the molecular weight is correctly obtained.

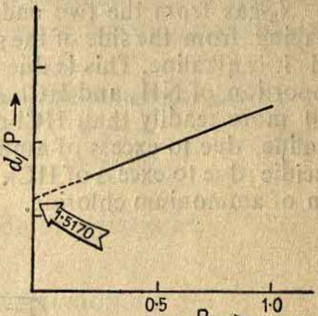


Fig. IV.5. *d*/*p* vs *P*

Problem : The normal density of phosphine at 0°C and at different pressures are :

P (atm)→	1	3/4	½	1/4
d/*p* (gm/litre)→	1.5307	1.5272	1.5238	1.5205

Calculate the mol. wt. of phosphine and at wt. of phosphorus.

From the extrapolation of *d*/*p* vs *P* curve to $P = 0$, the value of $(d/P)_0$ is found to be 1.5170 gm/litre.

$\therefore\ M = (d/P)_0 RT = 1.5170 \times .0821 \times 273 = 34.00$

The atomic wt. of phosphorus $\doteq 34 - 3 \times 1.008 = 30.98$

This problem clearly illustrates that the measurement of limiting density enables one to find out not only the molecular weight but sometimes atomic weight as well.

It should be realised that *d*/*p* is to be plotted against pressure. If density is plotted against pressure, the line would pass through the origin, as at zero pressure density is considered to be nil.

4.4. Abnormal densities

For certain substances such as ammonium chloride, nitrogen peroxide, phosphorus pentachloride, etc. the measured densities are found to be less than those calculated from their molecular formulae. The observed densities decrease towards a limit as the temperature is raised. This is due to the splitting of the molecules into simpler ones. The process is reversible and is called *thermal dissociation*. Examples:

$$NH_4Cl \rightleftharpoons NH_3 + HCl \qquad I_2 \rightleftharpoons 2I$$

$$N_2O_4 \rightleftharpoons 2NO_2 \qquad PCl_5 \rightleftharpoons PCl_3 + Cl_2$$

With increase in the number of molecules, the volume increases (pressure remaining constant) and, in consequence, the density decreases. As the temperature rises, more and more dissociation takes place, and when practically complete dissociation occurs the density reaches its lowest limit.

The occurrence of the thermal dissociation has been proved by the ingenious experiment devised by Than and Pebal. Some NH_4Cl is enclosed in a tube by the side of a porous partition made of compressed solid NH_4Cl. The tube is heated near the heap of NH_4Cl and a continuous slow current of N_2-gas is maintained in the tube on both sides of the partition (Fig. IV.6). The vapours coming out with the N_2-gas from the two ends are separately led into litmus solution. The gas escaping from the side of the solid NH_4Cl is found to be acidic while at the other end it is alkaline. This is due to the fact that NH_4Cl on dissociation gives equal proportion of NH_3 and HCl. Ammonia being lighter diffuses through the porous wall more readily than HCl-gas. So the gas coming out from the other side is alkaline due to excess of ammonia; the gas coming out from the side of NH_4Cl is acidic due to excess of HCl. It therefore conclusively demonstrates the dissociation of ammonium chloride.

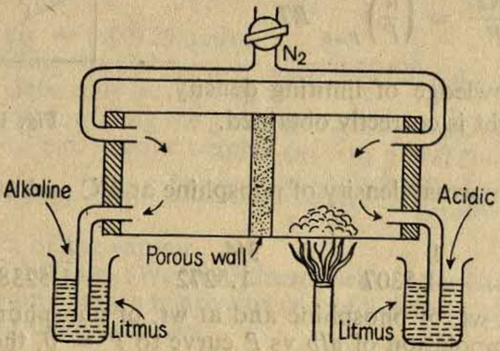


Fig. IV.6. Experiment of Than and Pebal

The extent of dissociation, *i.e.*, the fraction of the total number of molecules which suffers dissociation is called the *degree of dissociation*. Gas density measurements can be used to determine the degree of dissociation. Let us take a general case where one molecule of a substance *A* splits up into *n* molecules of *B* on heating;

$$A \longrightarrow nB$$

Initial moles $1 \quad 0$

After dissociation $1-\alpha \quad n\alpha$; Total no. of moles $= 1 + (n-1)\alpha$
where α is the degree of dissociation.

At equilibrium, for each mole of *A*, there will be $(1-\alpha)$ moles of undissociated *A* and $n\alpha$ moles of *B*. The total number of moles in the system would be $[1 + (n-1)\alpha]$.

Let *V* denote the volume of a mole of any gas at the temperature and pressure of the experiment. Since *P* and *T* are constant, the volume of the system would increase due to dissociation. Consequently density would decrease. If ρ_0 denotes the density assuming absence of dissociation and ρ denotes the observed density when actual dissociation has occurred, we have for the total weight of the gas,

$$W = \rho_0 V \quad \text{and} \quad W = \rho . V[1 + (n-1)\alpha]$$

i.e. $$\frac{\rho_0}{\rho} = 1 + (n-1)\alpha$$

(where *n* denotes the number of product molecules from each molecule of the reactant.)

Since densities (ρ) are proportional to vapour densities (D), then

$$\frac{D_0}{D} = 1 + (n-1)\alpha, \quad \text{or} \quad \alpha = \frac{D_0 - D}{(n-1)D} \qquad \ldots \text{(IV.2)}$$

This relation is used to calculate the degree of dissociation. It is implicit that pressure and temperature remain constant. D_0, the vapour density of undissociated reactant is half the molecular weight, M_0, or $D_0 = M_0/2$.

If M denotes the average molecular weight of the gases when the gas is partly dissociated, the equation (IV.2) can be written as $\alpha = \frac{M_0 - M}{(n-1)M}$ ... (IV.3)

Let us consider some examples.

(*i*) *Dissociation of* NH_4Cl: Ammonium chloride dissociates as,

$$\begin{array}{llll} NH_4Cl \rightarrow & NH_3 + & HCl & \\ 1-\alpha & \alpha & \alpha, & \text{Total moles: } 1+\alpha \end{array}$$

$$\therefore \quad \frac{D_0}{D} = 1 + \alpha \quad \text{or} \quad \alpha = \frac{D_0 - D}{D} \; ; (\text{since } n = 2)$$

(*ii*) *Dissociation of water vapour* at very high temperature

$$H_2O \rightarrow H_2 + \tfrac{1}{2}O_2, \text{ hence } n = 1.5$$

$$\therefore \quad \alpha = \frac{D_0 - D}{(1.5-1)D} = \frac{D_0 - D}{0.5D}$$

(*iii*) *Dissociation of iron carbonyl*

$$\begin{array}{llll} Fe(CO)_5 \rightarrow & Fe + & 5CO & \\ 1-\alpha & & 5\alpha, & \text{Total moles} = 1 + 4\alpha \end{array}$$

In estimating volumes, any solid or liquid product has to be ignored; hence '*n*' here is 5 instead of 6.

$$\therefore \quad \alpha = \frac{D_0 - D}{(5-1)D} = \frac{D_0 - D}{4D}$$

In dissociations, where there is no change in the number of molecules, there will be no net increase in volume and hence density will not change, as in the dissociation; $2HI \rightleftharpoons H_2 + I_2$. The degree of dissociation (α) in such cases cannot be obtained from density measurements.

The degree of dissociation of many substances like I_2, $COCl_2$, $SbCl_3$, PCl_5, SO_2Cl_2, etc. has been studied from vapour density measurements.

Problem: At 182°C, the vapour density of PCl_5 was found to be 72.25. Calculate its degree of dissociation.

$$D_0 = \tfrac{1}{2}M_0 = \tfrac{1}{2}(31 + 5 \times 35.5) = 104.25$$

$$D = 72.25$$

$$\begin{array}{lll} PCl_5 \rightarrow & PCl_3 + & Cl_2 \\ 1-\alpha & \alpha & \alpha = 1 + \alpha \end{array}$$

$$\therefore \quad \alpha = \frac{D_0 - D}{(2-1)D} = \frac{104.25 - 72.25}{72.25} = 0.44 \text{ or } 44\%$$

Problem: At 60°C, the density of N_2O_4 gas was found to be 30.2. Calculate the percentage of NO_2 molecules by weight and by volume.

$$N_2O_4 \rightarrow 2NO_2$$

$$1-\alpha \qquad 2\alpha = 1+\alpha$$

The calculated density of N_2O_4; $\rho_0 = M/2 = 46$

The observed density; $\rho = 30.2$

Hence $$\alpha = \frac{(\rho_0 - \rho)}{\rho} = \frac{46-30.2}{30.2} = 0.523$$

That is, the fraction of gm-moles of N_2O_4 decomposed $= 0.523$

Or, percentage of NO_2 molecules by weight $= 52.3\%$

Again, in the mixture, the ratio of gm-moles of NO_2 and N_2O_4 is $\frac{2\alpha}{1+\alpha} : \frac{1-\alpha}{1+\alpha}$

This is also the ratio of their volumes. Hence, percentage of NO_2 by volume

$$= \frac{2 \times 0.523}{1 + 0.523} \times 100 = 68.7\%$$

Problem: At 200°C, the vapour density of nickel carbonyl was 40.35. Calculate the degree of dissociation, (Ni = 58.7).

$$Ni(CO)_4 \rightarrow Ni + 4CO$$

$$D_0 = \tfrac{1}{2}M_0 = \tfrac{1}{2}[58.7 + 4 \times 28] = 85.35$$

Here $n = 4$; the volume of Ni is negligible.

$$\therefore \quad \alpha = \frac{D_0 - D}{(n-1)D} = \frac{85.35-40.35}{3 \times 40.35} = 37.2\%$$

Problem : 1.588 gm N_2O_4 was contained in a half litre flask at 25°C under a total pressure of 1 atm. Calculate α.

$$N_2O_4 \rightarrow 2NO_2$$

$$1-\alpha \qquad 2\alpha; \qquad \text{Total moles, } 1+\alpha$$

$$\therefore \quad Pv = n(1+\alpha)RT; \text{ mol. wt. of } N_2O_4 = 92.02$$

or $$1 \times \tfrac{1}{2} = \frac{1.588}{92.02}(1+\alpha) \times 0.082 \times 298$$

whence $$\alpha = 0.186 \text{ or } 18.6\%$$

Association : Sometimes the measured vapour-densities are observed to be higher than half the molecular weight (D_0). In such cases, the gas molecules remain associated to some extent. Such phenomena are found in acetic acid, NO_2, etc. They oten remain as dimers such as $(CH_3COOH)_2$. With increase in temperature dimers break up into monomers, when densities are reduced to their normal values.

EXERCISES

I

1. Explain the princple employed in determining the density of a gas by Buoyancy micro-balance.

2. Describe Victor-Meyer's method of determination of molecular weight of a substance. What are the limitations of this method?

3. Suggest two methods for determination of the mol. wt. of carbon tetrachloride and give a brief outline of those methods.

4. How would you proceed to find out the mol. wt. of ether by Duma's method?

5. Distinguish between absolute density and vapour-density of a gas. Why the former varies with temperature and the latter does not?

6. What methods would you suggest for the determination of vapour-density of (*i*) argon (*ii*) acetone (*iii*) carbon monoxide.

7. What is meant by the term, *degree of dissociation*? How can you find out the degree of dissociation of a gas?

8. Write brief notes on: (*i*) Limiting density (*ii*) Abnormal vapour density (*iii*) Buoyancy balance method of gas-density determination.

II

9. In a buoyancy microbalance, it was found that the loss of weight was the same when an unknown gas at 20 mm or oxygen gas at 25 mm are introduced separately. **[Ans. 40]**

10. In a Hofmann experiment 0.0662 gm of a liquid was introduced when mercury level dropped from 737 mm to 482 mm. The temp. was 99.5°C and the vapour occupied 70.2 c.c. Calculate the mol. wt. of the substance. **[Ans. 85.9]**

11. In determining the mol. wt. of chloroform by Hofmann method, the following data were obtained:

Weight of chloroform = 0.2704 gm volume of vapour = 113 ml
Barometric height = 747 mm height of Hg column = 285.2 mm
Temp. = 99.6°C.
Calculate the mol. wt. **[Ans. 120.3]**

12. Estimate the vapour density of a substance from the following: 0.16 gm of a substance on vaporisation displaced 26.2 c.c. of moist air at 17°C and 764 mm pressure. The aqueous tension at 17°C is 14 mm. **[Ans. 73.82]**

13. In a Victor Meyer's experiment, 13.5 c.c. air was displaced at 15°C and 750 mm pressure when 0.0623 gm vaporised. (f = 12.7 mm). Calculate its molecular weight. (Cal. Univ.) **[Ans. 48.3]**

14. 0.2335 gm substance was vaporised in a Victor Meyer's apparatus. At 29°C and 740 mm pressure, the volume of displaced air was 37.1 ml; aqueous tension at 29°C = 26.3 mm. What is its mol. wt.? (Travancore Univ.) **[Ans. 166.1]**

15. Calculate the mol. wt. of chloroform from the data as obtained from a Victor Meyer's experiment: 0.22 gm chloroform when vaporised displaced 45 c.c. of moist air measured at 20°C and 755 mm. Aq. tension at 20°C is 17.4 mm. **[Ans. 120.1]**

16. A saturated organic liquid composed of carbon, hydrogen and chlorine contained 70.9% by wt. of chlorine. When 0.21 gm of this liquid was vaporised in Victor Meyer's apparatus, the dry air displaced was 52.0 c.c. at a pressure of 756 mm and 24°C. Find out the mol. wt. and formula of the substance. **[Ans. 99; $C_2H_4Cl_2$]**

17. Calculate the mol. wt. of an organic compound from the following data obtained from Duma's method of determination.

At 20°C, the wt. of air-filled bulb = 49.433 gm
At 99°C, the wt. of vapour filled bulb = 49.848 gm
At 20°C the wt. of water-filled bulb = 161.2 gm
At 20°C the density of water = 0.998 gm/cc.
The normal density of air = 1.29 gm/litre **[Ans. 153.9]**

18. At 0°C, the limiting density of ammonia and hydrogen are 0.7599 and 0.089922 gm/litre. What is the atomic weight of nitrogen? [H = 1.008] **[Ans.** 14.008]

19. At 0°C, the limiting density of hydrogen bromide is 3.611 gm/litre. Estimate the at. wt. of bromine. **[Ans.** 79.917]

20. At 90°C, the vapour density of N_2O_4 was found to be 24.8 (H = 1). Calculate its degree of dissociation into NO_2 molecules. (C.U.) **[Ans.** 0.85]

21. At 520°C, the vapour density of phosphorus pentachloride is 57.92. Find out the extent of its dissociation. **[Ans.** 79.98 %]

22. (*a*) 1.5 gm of PCl_5 was completely vaporised at 144°C and occupied a volume of 410 c.c. at 1 atm. Calculate degree of dissociation.

(*b*) 0.1 gm of ammonium carbamate when vaporised at 100°C and 1 atm has a volume of 117 c.c. To what extent it is dissociated? **[Ans.** (*a*) 66% (*b*) 99.2%]

23. Find out the extent dissociation in each of the following: (*i*) The vapour density of steam is 8.8 at 1100°C, (*ii*) At 180°C, the vapour density of $Fe(CO)_5$ is 40.4.

[Ans. (*a*) 4.54% (*b*) 35.6%]

24. At 250°C, 4.5 gm PCl_5 was completely vaporised to a volume of 1700 c.c. under one atmosphere. Calculate its extent of dissociation. (C. U.) **[Ans.** 0.835]

CHAPTER 5

THE PROPERTIES OF LIQUIDS

5.1 The Liquid State

On cooling a gas changes into the liquid state and on further cooling the liquid freezes into the solid state. The liquid state is thus an intermediate one between the gaseous and the solid states. In fact, a liquid has some of the properties of gases and some of solids. Its very existence lies in the temperature range between the melting point of the solid and the condensation point of the gas. In the solid state, the molecules are present in a regular fixed pattern, there is a very strong cohesive force between the molecules and free translatory motion is absent. In the gaseous phase the molecules are in a chaotic state, the intermolecular cohesive force is small and the molecules are in random chaotic motion. From the standpoint of the kinetic theory, a liquid is a transition of the gas-phase into a region of strong intermolecular cohesive forces which help to keep it in a smaller and definite volume. But the molecules are still mobile to some extent and are not rigidly fixed.

In melting, the density or volume of the liquid does not appreciably alter from that of its solid state. That is, cohesive force does not decrease much. Again the latent heat of fusion is much less than the latent heat of vaporisation, *i.e.*, the increase in internal energy due to fusion is relatively small. The low latent heat of fusion also suggests small decrease in intermolecular cohesive force. This is further supported by the fact that the specific heats of a substance in its solid and liquid state approach each other near the melting point. The other resemblance between the solid and the liquid state is their relative low compressibility compared to gases.

On the other hand, the lack of rigidity is the most notable resemblance between the liquids and the gases. A liquid or a gas can offer no permanent resistance to a shearing stress. The comparative ease with which liquids flow or diffuse indicates that some gas-like disorder exists in them. In a gas we find the maximum disorder or chaos, whereas in a crystal there is perfect well-ordered arrangement of its molecules. It is reasonable to presume from the above facts, that inspite of some disordered motion of some molecules, there must be present also some amount of ordered arrangement. There might be clusters of molecules with some ordered pattern embedded in a mass of chaotically moving molecules. The introduction of thermal energy increases the disorder. The liquid may hence be considered to have a complex structure like that of a crystal except that well-ordered pattern extends over a short range instead of over the entire mass. X-ray diffraction studies confirm this.

For the presence of complex molecular configuration, a precise mathematical formulation of a theory to explain the behaviour of liquids like the one for gases has not yet been developed.

van der Waals Forces : The intermolecular attractions or cohesive forces, are responsible for the liquid state, as otherwise the kinetic energy would have dispersed the molecules into a gas. The intermolecular forces, in general, are called van der *Waals* forces'. The van der Waals forces arise due to the following causes:

(*a*) *Dipole-dipole interaction* : When the molecules are polar, they have an electrically positive and an electrically negative centre within (see dipole moment). Due to electrostatic attraction, the polar molecules or dipoles orient themselves in proper fashion and remain thus grouped or associated.

(*b*) *Dipole induced dipole attraction* : Besides, a dipole will always cause polarisation in the neighbouring molecules when the attractive forces would be still more strong. Even if the dipole be in the vicinity of a non-polar molecule, the latter would be polarised and then the induced dipole would be attracted.

(*c*) *Dispersion forces* : Attractive forces exist even between non-polar molecules. Due to the oscillations of the electron clouds with respect of the nuclei of atoms in a molecule, tiny instantaneous polarity is created. These small dipoles induce dipole moments in the neighbouring atoms or molecules and then attraction arises between them. Such forces of attraction are called 'dispersion forces'. The measured non-polarity of the molecule is a time-average property of the fluctuating tiny dipoles.

In the liquefaction of non-polar substances, only the dispersion forces take part. But for polar substances all the effects contribute to van der Waals interaction for liquefaction.

When the molecules come in close proximity, the electron atmospheres as well as the nuclei of the atoms would repel one another and a *repulsive force* also comes into play. This, however, helps in maintenance of the individuality of the molecules.

5.2. Liquefaction of Gases

Lowering of temperature (cooling) and increase of pressure (compression) are required for liquefying gases. Of these two, the cooling is more important. Since the time of Andrews experiments, it is known that a gas can be liquefied only if it be below its critical temperature. Even then, high pressures have often to be employed. The lower the temperature, lesser would be the required pressure.

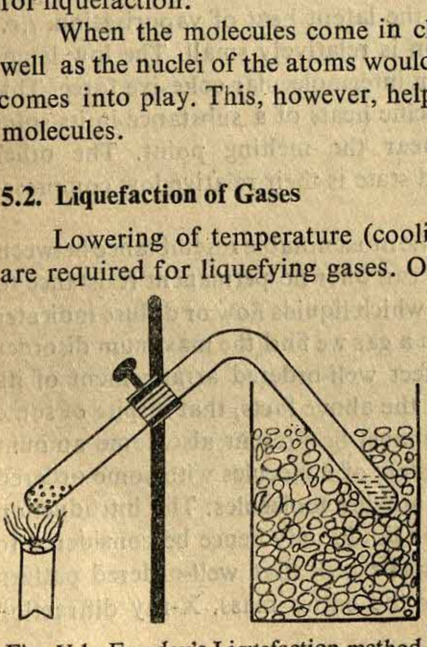
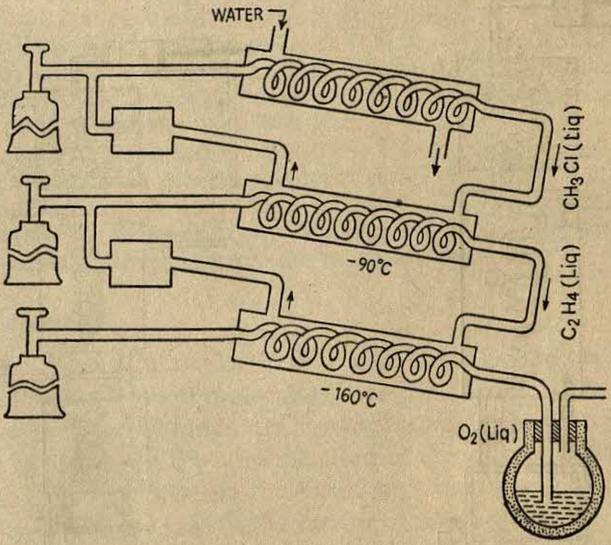


Fig. V.1. Faraday's Liquefaction method

Systematic researches in liquefaction of gases began from 1823 when Faraday succeeded in liquefying gases like chlorine, sulphur dioxide, ammonia, hydrogen chloride etc. Faraday's method consisted of generating the gas at one end of a sealed inverted V-tube, the other end being kept immersed in a refrigerant (Fig. V.1). But gases like hydrogen, nitrogen, oxygen etc. resisted liquefaction by this method. By the end of the nineteenth century Pictet developed the *method of cascades*. K. Onnes (1894) succeeded in liquefying oxygen by this method.

Methyl chloride (T_c, 416°K) was liquefied at ordinary temperature by compression. When liquid methyl chloride was allowed to evaporate off at a reduced pressure, the temperature dropped to −90°C. Ethylene gas under compression was passed through a spiral tube immersed in the evaporating liquid methyl chloride. Ethylene liquefied. The liquid ethylene is next allowed to pass through the annulus of a condenser under reduced pressure where it vaporises and lowers the temperature to −160°C. Oxygen is now passed through the inner-tube of this condenser under pressure. The oxygen liquefied at this temperature which is below its critical temperature, −119°C. This illustrates the method of cascades (Fig. V.2).



Fig, V.2. Liquefaction by cascade method

From the technical point of view the following steps are taken for liquefaction of gases.

(1) The gas must be under its critical temperature.

(2) High Pressure is employed to compress the gas. The lower the temperature, lesser would be the required pressure. The heat of compression is removed by passing the gas through tubes surrounded by refrigerants.

(3) Cooling by Joule-Thomson adiabatic expansion from a very high pressure to a low pressure through a valve.

(4) Lowering of temperature is also achieved by performance of external work by the gas on an engine.

(5) The uncondensed outgoing cooled gas is used to further cool down the incoming gas.

Joule-Thomson Cooling effect: When a cooled gas is allowed to pass through a narrow valve from a high pressure to a low pressure under adiabatic conditions, the temperature falls. This is Joule-Thomson cooling. For every gas, there is a temperature called *Inversion temperature* (T_i). The *J-T* cooling takes place only below its inversion temperature. Hence, the gas must be at a temperature below its T_i, for cooling. The lower the temperature of the compressed gas, the greater will be the fall in temperature in Joule-Thomson expansion.

At 0°C, the *J-T*, cooling per atmosphere of pressure drop:

1.46° for CO_2 ; 0.31° for Nitrogen ; 0.326°C for oxygen

The outline of two processes for liquefaction of air is given here.

In the Linde's process, dry air is first compressed to a high pressure, say 100 atm. in *A* (Fig. V.3) and it is then passed through a coil surrounded by a refrigerant (*B*), say evaporating ammonia or sulphur dioxide so that the heat of compression is removed. The relatively cooled gas then passes through the coil *C* and finally it expands through a throttle *E* from a pressure of 100 atm. to nearly 1 atm. This Joule-Thomson expansion immediately lowers the temperature considerably. This expanded gas is used to cool the incoming gas in chamber *C* and is recirculated to the high-pressure line. The lower the temperature of the incoming gas at *E* the lower will be the *J-T* cooling. Repetition of the cycle ultimately lowers the temperature to such an extent that on passing the valve *E*, the gas is transformed into the liquid.

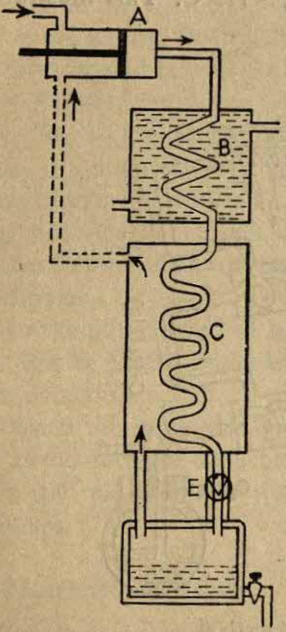


Fig. V.3. (Linde)

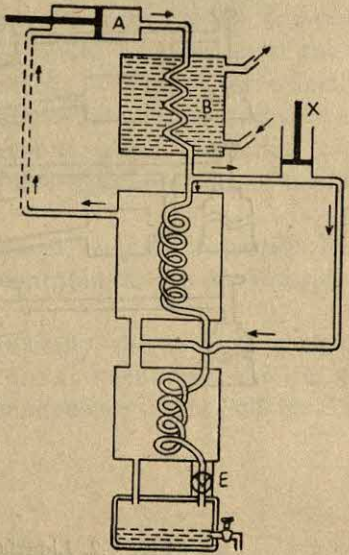


Fig. V.3a (Claude)

The efficiency of the method is considerably increased in the Claude process, in which the compressed and cooled gas emanating from *B* is made to work against a piston (*X*) of an engine under adiabatic conditions (Fig. V.3a). This adiabatic work is performed at the expense of the internal energy of the gas and hence there would be a fall in temperature. The work received is at least partly utilised in the compression engine *A*. The rest of the Claude's process is similar to that of the Linde's.

The liquefaction of hydrogen and helium proved very difficult due to their intermolecular forces being very small and their inversion temperatures very low. Dewar succeeded in liquefying hydrogen for the first time by cooling it to −200°C using Linde's regenerative cooling process and using liquid air evaporating at very low pressures as refrigerant. Hydrogen thus cooled was made to suffer *J-T* expansion through a nozzle when the gas liquefied. Helium was liquefied by K. Onnes (1898) by a similar process using liquid hydrogen as evaporating refrigerant. Kapitza (1934) liquefied both hydrogen and helium.

When helium was solidified (Keesom 1926), the attention of the physicists was directed towards attaining still lower temperature. The race towards absolute 0°K (experimentally unrealisable) was rendered possible by the discovery of a new principle called *adiabatic demagnetisation* of para-magnetic salts first suggested by Debye and by Giauque independently in 1926. Using this principle, it has been possible to reach as low a temperature as 0.001°K. Subsequently nuclear demagnetisation moved this limit further to 0.00001°K.

Liquified gases have varied applications. For example, (*a*) liquid air is the source of oxygen required in rockets, jet planes etc. (*b*) liquid ammonia and sulphur dioxide are used as refrigerants (*c*) liquid ammonia is also directly injected into soil as fertiliser (*d*) liquid chlorine is used for bleaching and disinfectant purposes (*e*) liquid CO_2 is often utilised in preparation of drinks, etc.

5.3. Vapour Pressure

If a liquid be placed in a closed vessel with some free space above it, there would be a continuous flight of molecules from the liquid surface into the free space. At the same time, the randomly moving molecules of vapour return to the liquid surface depending on the concentration of the vapour. And finally a state of equilibrium is reached between the liquid and the vapour when the rate of escape from the surface is equal to the rate of condensation of the vapour. At a given tmperature, a definite pressure of the vapour is reached under such conditions of equilibrium. This pressure at which liquid and vapour can coexist is the *saturation vapour pressure*, or simply, *vapour pressure* of the liquid at the given temperature. The vapour pressure depends only on the temperature and is independent of the quantity of liquid or the space occupied by the vapour.

The vapour pressure can be easily measured with the help of an isoteniscope or by introducing the liqiud in the Torricelli's space in a mercury barometer. A portion of the liquid vaporises and depresses the mercury of the barometric tube. The height through which the mercury level falls gives the vapour pressure at the temperature maintained.

The vapour pressure of all liquids increases with rise in temperature. The quantitative dependence of vapour pressure on temperature can be empirically represented as

$$\log p = \frac{A}{T} + B \qquad \ldots (V.1)$$

where *A* and *B* are constants. It means that the plots of $\log p$ vs $\frac{1}{T}$ shall be linear.

This has been confirmed from experimental results (Fig. V.4). The equation (V.1) can be obtained from thermodynamical considerations (see Clausius-Clapeyron equation).

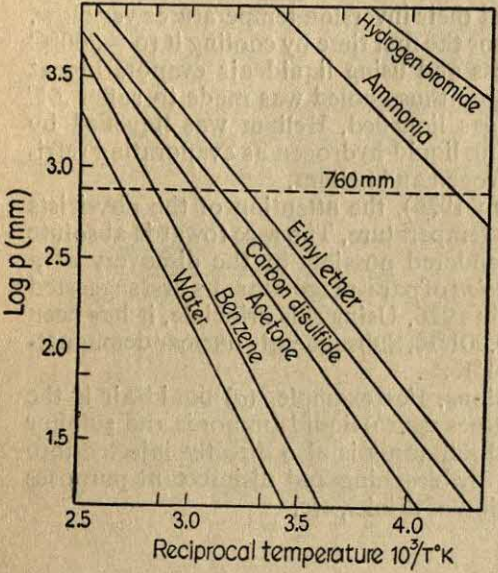


Fig. V.4. log p vs $\frac{1}{T}$

When the liquid boils, that is, its vaporisation takes place throughout the bulk and not only from the surface, the vapour pressure becomes equal to the superincumbent pressure. Under normal conditions of atmospheric pressure, the vapour pressure would be 760 mm when the liquid boils. Or, every liquid would boil at the temperature when its vapour pressure is one atmosphere.

Trouton's Rule: This rule relates the boiling point and heat of vaporisation of a liquid, expressed as

$$\frac{\triangle H}{T_b} \approx 21 \text{ (cal °K}^{-1} \text{ mole}^{-1}) \quad \ldots (V.2)$$

where $\triangle H$ is the molar heat of vaporisation at its boiling pt.T_b°K. That is, from a knowledge of the b. pt, the latent heat can be approximately guessed. This rule is generally obeyed by non-polar liquids. But considerable departure is observed in cases where the liquids consist of highly polar molecules and remain often associated (see Sec. 11.5).

Boiling Point Rule : There is another emipirical rule which suggests that the ratio of boiling temperature (T_b°K) and the critical temperature (T_c°K) is approximately 0.67 for most of the liquids.

$$T_b/T_c \approx 0.67 \quad \ldots (V.3)$$

This is called *Guldberg Rule*. It is generally found to be true but mercury and helium deviate considerably.

Example : The boiling point of benzene is 80.1°C. Estimate roughly the heat of its vaporisation per gm and its critical temperature.

$$T_c = \tfrac{3}{2} T_b = \tfrac{3}{2}(273 + 80.1) = 529.7\text{°K}$$

$$\triangle H_{vap} = 21 \times T_b = 21 \times 353.1 = 7415.1 \text{ cal mole}^{-1}$$

$$\therefore \quad \triangle H_{vap} = \frac{7415.1 \text{ cal mole}^{-1}}{78 \text{ gm mole}^{-1}} \approx 97.8 \text{ cal/gm}$$

5.4. Surface Tension

Consider a liquid in contact with its vapour. A molecule in the bulk of the liquid is subjected to forces of attraction from all directions by the surrounding molecules and is practically in a uniform field of force. But for a molecule at the surface, the net attraction towards the bulk of the liquid is much greater than that towards the vapour where the attracting molecules are more widely dispersed (Fig. V.5) This means that the molecules at the surface are pulled inwards. The result is liquid surfaces in absence of other forces tend to contract to minimum areas. The surface layer seems to behave as a stretched membrane and this psuedo-membrane tends to contract. It explains why a small amount of liquid, left freely, such as mercury, rain drop, etc. always takes spherical shape; because the sphere, for a given volume, has the least surface area.

That there is such a pull on the molecules of the surface layer can be easily demonstrated. If a circular copper-wire ring having a silk-thread tied loosely to the two opposite points be dipped into a soap solution so that on withdrawal a thin film stretches across the entire ring, the thread will freely swim in the film being attracted in all directions (Fig. V.5a). But if the film is punctured in one part, say A, the thread will be pulled now in the direction of B only (Fig. V.5b) where the film is intact. The thread will immediately assume the most-stretched position.

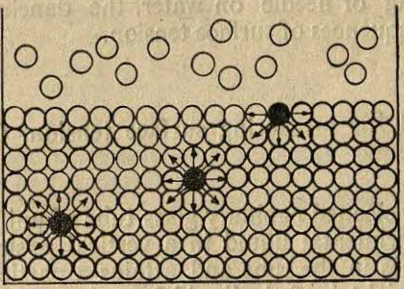


Fig. V.5

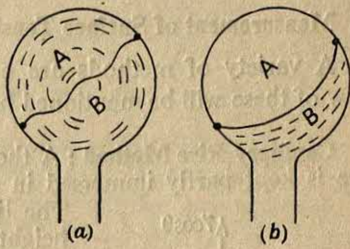


Fig. V.5a, 5b

Now, since the surface is in a state of tension, an attempt to make a penetration along any line in the surface will require an application of force to pull apart the separate portions of the surface. This force is called the *surface tension*, denoted usually by the symbol γ. It is expressed as the force in dynes per unit length acting at right angles to the line along the surface of the liquid.

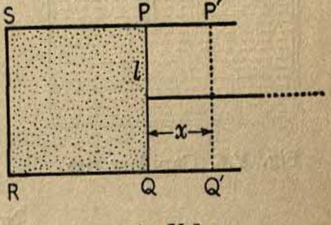


Fig. V.5c

Any increase in the area of the surface of a liquid against its natural tendency to contract will require performance of work. Consider a liquid film *PQRS* contained in a rectangular wire-frame, in which the side *PQ* is movable (Fig. V.5c). Suppose now the film is stretched by moving the boundary *PQ* by x cm to $P'Q'$. The length of *PQ* is l cm, If γ be the surface tension acting per cm, the force acting towards the film is $\gamma.2l$. It is to be remembered that there are two surfaces of the film.

The work done in stretching the film,

$$W = \gamma.2l \times x = \gamma.2xl = \gamma.\triangle A$$

or

$$\gamma = \frac{W}{\triangle A}$$

$\triangle A$ is the total area of the new surfaces created on the two sides of the film.

The work (ergs) necessary to create or extend one sq. cm. of surface area is called the *surface energy* of the liquid per sq. cm. In other words, the surface tension is numerically the same as the surface energy per unit area of the liquid. The total surface energy is obtained by multiplying the surface tension of the liquid by its area.

The rise of liquids in capillary tubes, the suction of ink by blotting paper, the removal of dirt by soap soln., the floating of needle on water, the dancing of camphor on water surface, etc. are all consequences of surface tension.

5.5. Measurement of Surface Tension

A variety of methods are employed for measuring surface tension. Only a few of these will be mentioned here.

Capillary Rise Method : A thoroughly cleaned capillary glass tube of uniform bore is kept partly immersed in the experimental liquid in a vertical position. The liquid rises in the tube and attains a particular height. The height h of the liquid from the surface of the bulk outside to the bottom of the meniscus (Fig. V.6) is carefully measured with a travelling microscope. The radius r of the capillary tube is predetermined by the usual method of inserting a pellet of mercury and measuring its length and weight.

The upper meniscus is concave and if θ be the angle of contact then, the vertical component of the surface tension (γ) will be $\gamma \cos \theta$. The contact line of the meniscus with the wall of the tube is $2\pi r$. Hence the net upward pull is $2\pi r\gamma\cos \theta$. This is balanced by the weight of the liquid which has been drawn up. The weight of the liquid column is $(\pi r^2 h + v)\rho g$, where v is the volume of the liquid in the curved meniscus itself, and ρ is the density of the liquid. Then,

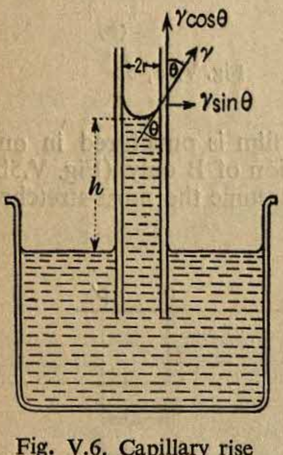


Fig. V.6. Capillary rise

$$2\pi r\gamma \cos \theta = (\pi r^2 h + v)\, \rho g$$

The radius of curvature of the concave meniscus may be taken to be the same as the radius of the capillary tube.

So, $$v = \pi r^3 - \tfrac{2}{3}\pi r^3 = \tfrac{1}{3}\pi r^3$$

Substituting, $$2\pi r\gamma \cos \theta = (\pi r^2 h + \tfrac{1}{3}\pi r^3)\, \rho g$$

or $$\gamma = \frac{r\rho g(h + \frac{1}{3}r)}{2 \cos \theta} \qquad \ldots (V.4)$$

Often θ is found to be nearly zero, so that $\cos\theta \approx 1$, hence

$$\gamma = \frac{r\rho g(h + \frac{1}{3}r)}{2} \text{ dynes/cm} \qquad \ldots (V.5)$$

Thus, the measurement of h and r with a knowledge of the density ρ will enable us to determine the surface tension. Various precautions are of course taken in making the measurements.

Since r is quite small, the commonly used expression is

$$\gamma = \tfrac{1}{2} r\rho g h \qquad \ldots (V.5a)$$

Double Capillary Method: When the quantity of the experimental liquid available is not large, two capillaries of different diameters (predetermined, say 2 mm and 0.5 mm) are partially dipped side by side (Fig. V.6a). The difference in heights of the capillary rise ($\triangle h$) is measured. The density is also measured. Using eqn. (V.5a),

$$\frac{\gamma}{r_1} = \tfrac{1}{2}\rho g h_1 \quad \text{and} \quad \frac{\gamma}{r_2} = \tfrac{1}{2}\rho g h_2$$

$$\therefore \; \gamma \Big/ \left(\frac{1}{r_1} - \frac{1}{r_2}\right) = \tfrac{1}{2}\rho g \triangle h \qquad \ldots (V.5b)$$

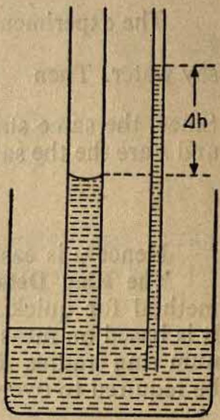


Fig. V.6a

The surface tension γ is then easily obtained as $\triangle h$, ρ, r_1 and r_2 are known.

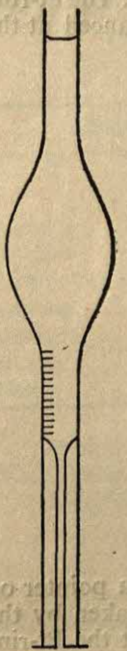


Fig. V.6b
Stalagmometer

Drop Weight Method : When a drop of liquid is at the point of being detatched from the circular end of a vertical capillary tube, the upward and downward forces must balance one another. The upward force is $2\pi r\gamma$. The downward force consists of the weight of the liquid drop and the excess pressure inside the drop, which has a curved surface. The excess pressure inside the drop is $\frac{\gamma}{r}$.

Hence, the total downward force $= mg + \pi r^2 . \frac{\gamma}{r}$

At equilibrium, $2\pi r\gamma = mg + \pi r^2 . \frac{\gamma}{r}$

or $\qquad \gamma = \frac{mg}{\pi r}$; (m = mass of the drop)

The determination of the weight of a liquid drop and the radius of the capillary mouth would give the desired surface tension.

The relation is not so simple; it is usually modified with a correction factor, ϕ, depending on the volume of the drop and the capillary-diameter. So,

$\gamma = \frac{mg}{r} . \phi = \frac{v\rho}{r}\phi$, where v = volume of a drop and ρ is its density.

This relation is often used to compare the relative surface tensions of two or more liquids. A pipette-like tube (Fig. V.6b), called *Stalagmometer*, having a very smooth capillary end is used for the purpose. The tube is thoroughly cleaned and the experimental liquid is sucked in. The apparatus is kept in a vertical position in an enclosure free from disturbances or air currents. The liquid is allowed to drop very slowly, ensuring that every drop is fully formed. A definite volume of the liquid (say V. c.c.) determined by marks in the stalagmometer is allowed to come out and the number of drops (n) counted. The density of the liquid is separately determined Then,

$$\gamma = \frac{(V/n)\rho}{r}\phi$$

The experiment is repeated with a second liquid of known surface tension γ', say water. Then

$$\gamma' = \frac{(V/n')\rho'}{r}\phi$$

Since, the same stalagmometer is used and the external factors are unaltered, V and r are the the same and ϕ is assumed to be the same, *i.e.*,

$$\frac{\gamma}{\gamma'} = \frac{n'\rho}{n\rho'}$$

Hence γ is easily calculated as γ' is known.

The Ring Detatchment Method (du Nouy) : This is now a commonly used method for quick determination of surface tension with appreciable accuracy. It is based on measurement of the force P, required to detatch a horizontal platinum ring (radius R) from the surface of the experimental liquid. The force will be required to overcome the pull due to surface tension. So,

$$P = 4\pi R\gamma, \ i.e., \ \gamma = \frac{P}{4\pi R} \qquad \ldots (A)$$

The apparatus used is the du Nouy's torsion balance (Fig. V.6c). The Pt-ring is thoroughly cleaned and suspended from the hook of the beam balanced at the other end by the torsion-wire. One end of the torsion wire carries a pointer on a circular scale and is previously calibrated with known weights taken by the beam. In a flat dish, the liquid is taken and placed in such a way that the Pt-ring just touches the surface. The knob of the torsion wire is then slowly turned until the ring is just detatched from the surface, keeping the beam always in horizontal position. The reading of the pointer gives the force P just at the moment of detatchment of the ring from the liquid surface. The magnitude of γ is then evaluated from equation (A).

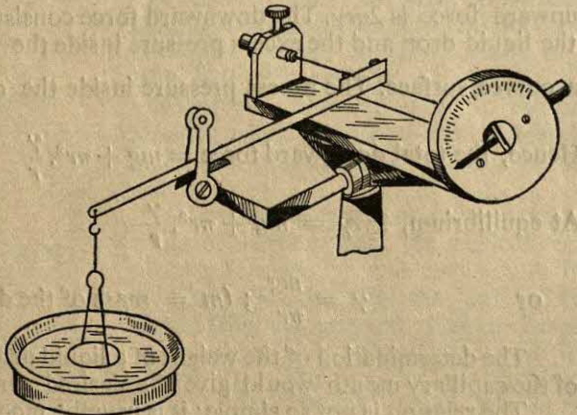


Fig. V.6c —du Nouy torsion balance

5.6. Surface Tension and Temperature

If M be the mol. wt. and v be the specific volume of a liquid, then the molar surface of a liquid assuming it to be a spherical mass is proportional to $(Mv)^{2/3}$. The molar surface energy is $k_1\gamma(Mv)^{2/3}$; k_1 is a constant and γ, surface tension. Eötvös established that the molar surface energy bears a linear relation to temperature, expressed as,

$$\gamma(Mv)^{2/3} = k(t_c - t) \qquad \ldots \text{(V.6)}$$

where t_c is the critical temperature.

Ramsay and Shields improved the relation from innumerable experiments. The molar surface energy and temperature relation is now given as

$$\gamma(Mv)^{3/3} = k(t_c - t - 6) \qquad \ldots \text{(V.7)}$$

where k is called the Eötvös constant. For non-polar normal liquids, k has a value of 2.1. For the associated liquids, like water, acetic acid, etc., the values of k are found to be smaller than 2.1.

The constant is evaluated by measuring surface tensions and specific volumes (from density) at two temperatures, for

$$k = \frac{\gamma_2(Mv_2)^{2/3} - \gamma_1\,(Mv_1)^{2/3}}{t_1 - t_2}$$

The surface tension values of some common liquids are given here.

SURFACE TENSIONS OF SOME LIQUIDS IN DYNES/CM

Liquids	*Temperature* (°C)			
	0°	20°	40°	60°
Benzene	31.6	28.9	26.3	23.7
Toluene	30.7	28.4	26.1	23.8
Carbon Tetrachloride	—	26.8	24.3	21.9
Acetone	26.2	23.7	21.2	18.6
Methanol	24.5	22.6	20.9	—
Ethanol	24.05	22.27	20.6	19.01
Water	75.64	72.75	69.56	66.18

Problem : A capillary tube of internal diameter 0.2 mm is dipped into water when water rises 15 cm. Calculate surface tension of water.

Neglecting curvature and assuming that angle of contact is zero, ($r = 0.01$ cm),

$$\gamma = \frac{rh\rho g}{2} = \tfrac{1}{2}\,(0.01 \times 15 \times 1 \times 981) = 73.6 \text{ dynes/cm}$$

5.7. Parachor

Macleod proposed an empirical relation between surface tension of a liquid (γ) and its density (D), in the form

$$\frac{\gamma^{\frac{1}{4}}}{D-d} = C \text{ (constant)}, \quad \text{where } d = \text{density of vapour}$$

Multiplying both sides by M, the mol. wt. of the substance,

$$\frac{M\gamma^{\frac{1}{4}}}{(D-d)} = M.C = P \text{ (constant)}; \qquad \ldots \text{(V.8)}$$

since M is also constant for a given substance.

It is remarkable that the constant P, called the *parachor*, is quite independent of temperature (Sugden, 1924). If the vapour density d, which is quite small, be ignored, then

$$P = \frac{M}{D} \cdot \gamma^{\frac{1}{4}} = V_m \gamma^{\frac{1}{4}}\ ; \quad V_m = \text{molar volume of the substance}$$

If at suitable temperatures, the surface tensions of two liquids be equal then their parachors would be proportional to their molar volumes. Further at a temperature where the surface tension of a liquid tends to unity, parachor is the measure of the molar volume. It was soon found that (*i*) parachors of many isomeric substances were identical and (*ii*) the difference in parachor-values of successive members in a homologous series was constant, irrespective of the nature of the series.

TABLE: PARACHORS

Isomers	P	*Homologous series*					
		Hydrocarbons			*Esters*		
			P	ΔP		P	ΔP
Amyl formate	293.6	C_2H_6	110.5		$C_2H_4O_2$	138.1	
Ethyl butyrate	293.6	C_3H_8	150.8	40.3	$C_3H_6O_2$	177.3	39.2
Butyl acetate	295.0	C_4H_{10}	190.0	39.2	$C_4H_8O_2$	216.1	38.8
Propyl propionate	295.0	C_6H_{14}	270.1	40.0×2	$C_6H_{12}O_2$	293.8	38.8×2
Ortho-xylene	283.3	C_7H_{16}	309.3	39.2	$C_7H_{14}O_2$	332.3	38.5
Meta-xylene	283.3						
Para-xylene	283.3						

It leads to the inescapable conclusion that parachors are additive functions of the chemical composition. The contribution of a CH_2-group to the parachor value is about 39. The molar parachor would be the sum of the atomic parachors. On this assumption, the parachor value of hydrogen, P_H, would be,

$$P_{C_nH_{2n+2}} = nP_{CH_2} + 2P_H = 39n + 2P_H$$

Substituting the experimental value of the parachor of the paraffin C_nH_{2n+2}, the atomic parachor *i.e.*, parachor equivalent of a hydrogen atom was found to be 17.1. So, the atomic parachor of a carbon atom is

$$P_C = P_{CH_2} - 2P_H = 39 - 2 \times 17.1 = 4.8$$

In this way, the parachor-equivalents of different atoms have been calculated (see Table below).

The parachors are not only additive but also constitutive. The double bonds, ring structures etc. make definite contributions to the parachor value of a compound. The parachor equivalent of a single bond is zero and those for other bonds and rings are given in the table below:

TABLE: ATOMIC AND STRUCTURAL PARACHOR EQUIVALENTS

Element	—	*P*	*Element*	—	*P*	*Structure*	—	*P*
C	—	4.8	S	—	48.2	Double bond	—	23.2
H	—	17.1	Cl	—	54.3	Triple bond	—	46.6
N	—	12.5	Br	—	68.0	6-membered ring	—	6.1
O	—	20.0	I	—	90.0	5-membered ring	—	8.5
P	—	39.2	O_2 in ester	—	60.0	4-membered ring	—	11.6
						Naphthalene ring	—	12.2

We can now illustrate the usefulness of parachor studies in the elucidation of molecular structures.

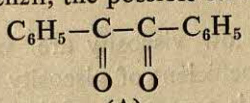
Structure of Benzene: The observed parachor of benzene is 206.2. If Kekule formula be accepted, its parachor value may be calculated as

6 C-atoms $= 6 \times 4.8$
6 H-atoms $= 6 \times 17.1$
1 six-membered ring $= 6.1$
3 double bonds $= 3 \times 23.2$

Total $P = 207.1$

The Kekule structure is thus supported.

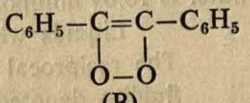
The parachor evidence had also been quite helpful as an additional support in cases where controversial structures were proposed from chemical reactions. Thus, for benzil, the possible structures are:



$C_6H_5-C(=O)-C(=O)-C_6H_5$

(A)

$P_{calc.} = 476.0$



$C_6H_5-C(-O-O-)=C-C_6H_5$

(B)

$P_{calc.} = 464.4$

Since the experimental value is 480, the structure (A) is favoured.

5.8. Viscosity

Viscosity is a property which opposes the relative motion of adjacent layers of flowing liquids. It is indeed an internal friction or resistance.

When a liquid is flowing steadily over a fixed horizontal surface (*i.e.*, the flow is streamline), its layer in immediate contact with the fixed surface is stationary and the velocity of layers increases with the distance from the fixed surface (Fig. V.7).

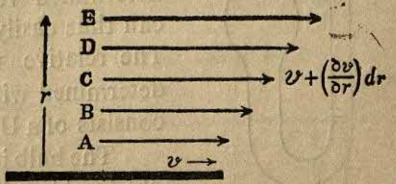


Fig. V.7

Select any layer; the layer immediately beneath will try to retard it while the layer above will accelerate it. Thus there is a tendency to destroy the relative motion as if there is a tangential force dragging backwards. This is the viscous force. Newton showed that this force of internal friction 'f' is directly proportional to the area of contact 'A' and the velocity gradient $\frac{dv}{dr}$.

Hence, $$f = -\eta A\frac{dv}{dr} \qquad \ldots (V.9)$$

The negative sign is indicative of the fact that the force is opposite to the direction of flow.

The proportionality constant η is called the *coefficient of viscosity.*

When $A = 1$, and $dv/dr = 1$, then $\eta = -f$

Hence we can define the 'coefficient of viscosity' as the tangential force required per unit area to maintain unit difference of velocity between two layers unit distance apart. The coefficient of viscosity is expressed in units of *poise*, which in *cgs* system is dynes-sec per sq. cm.

The flow of fluids through narrow tubes has been extensively studied. It is found that under a constant pressure-head p, the volume of liquid (v) coming out of a capillary tube of a radius (r) and length (l) in time t is given by Poiseuille's equation,

$$v = \frac{\pi p r^4 t}{8\eta l} \qquad \ldots (V.10)$$

Or $$\eta = \frac{\pi p r^4 t}{8 v l} \qquad (V.\ 11)$$

The quantities on the right hand side are measured and η is known. Thus at 20°C the viscosity of water is 10.09 millipoise.

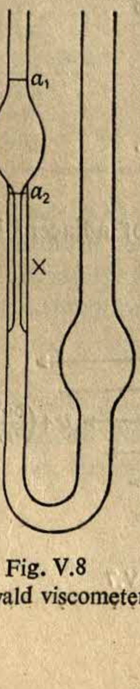


Fig. V.8
Ostwald viscometer

Liquids which have low viscosity are very mobile. The reciprocal of the coefficient of viscosity (η) is called **fluidity**, denoted by ϕ. It is a measure of the easy mobility of the liquid,

$$\phi = 1/\eta$$

Determination of viscocity.

(*i*) *Relative viscosity.* It is often quite convenient to determine the relative viscosity of a liquid, say with respect to water. The absolute viscosity of water has been determined very accurately at various temperatures. We can thus easily obtain the true viscosity of a given liquid. The relative viscosity for ordinary liquids is commonly determined with the help of the Ostwald viscometer. It consists of a U-tube as shown in Fig. V.8.

The bulb in the wider limb of the tube is first filled with the liquid and the liquid is then sucked up in the narrower limb up to the level a_1. The liquid then flows down the capillary X and the time θ_1 required to fall from level a_1

to a_2 is carefully noted. The experiment is repeated with water in the same tube and the corresponding time (θ_2) is also noted. Obviously,

$$\text{for the liquid,} \qquad \eta = \frac{\pi h \rho_1 g r^4 \theta_1}{8lv}$$

$$\text{and for water,} \qquad \eta_w = \frac{\pi h \rho_w g r^4 \theta_2}{8lv}$$

$$\text{or} \quad \frac{\eta}{\eta_w} = \frac{\rho_1 \theta_1}{\rho_w \theta_2}, \quad \text{or} \quad \eta = \eta_w \frac{\rho_1 \theta_1}{\rho_w \theta_2} \qquad \ldots \text{(V.12)}$$

The density of the liquid and the density of water are separately determined with the help of a pyknometer. Adequate precautions must be taken to maintain constant temperature (by using a thermostat) and the tube must be thoroughly cleaned before use.

(*ii*) *Falling sphere viscometer :* It was shown by Stokes that when a spherical body of radius r moves with a constant terminal velocity u through a medium having coefficient of viscosity η, then the driving force (f) which just balances the frictional resistance is given by the relation,

$$f = 6\pi\eta r u$$

If the spherical body falls under gravity, then

$$f = (4/3)\,\pi r^3 (d - d_l) g$$

where d and d_l are the densities of the solid sphere and the liquid respectively.

$$\text{Hence,} \qquad 6\pi\eta r u = (4/3)\pi r^3 (d - d_l) g$$

$$\text{or} \qquad u = \frac{2}{9} \frac{r^2 (d - d_l) g}{\eta} \qquad \ldots \text{(V.12a)}$$

This is Stoke's law.

Evidently if we can measure the velocity of a spherical ball moving down through a vertical column of the liquid it would be easy to know the viscosity of the medium.

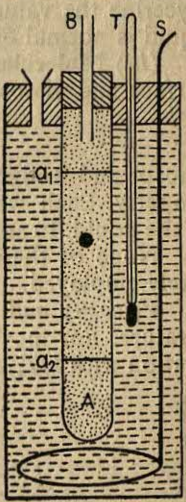


Fig. V.9

An apparatus of the type shown in Fig. V.9 is used for the purpose. The tube is filled with the liquid under investigation. Small steel balls, having diameter of 2-3 mm. are dropped through the narrow opening at *B*. The time θ taken by a ball to travel from a_1 to a_2 is noted by a stop-watch. The velocity (u) is given by length a_1a_2/θ. The coefficient of viscosity is then calculated from the equation (V.12a). The tube *A* is kept in a large cylinder of water provided with a thermometer and a stirrer to maintain constant temperature.

The viscosities of some common liquids are given in the Table below:

VISCOSITIES IN MILLIPOISES AT 20°C

Water	10.95	Chloroform	5.63
Ethanol	11.94	Carbon Tetrachloride	9.58
Methanol	5.93	Chlorobenzene	6.37
Acetone	3.31	Nitrobenzene	19.80
Ethyl ether	2.45	Benzene	6.47
Acetic acid	12.22	Glycerine	106.90

Some empirical relations concerning viscosity of liquids have been developed; some of these are mentioned here.

(*i*) **Rheochor :** Newton Friend showed that the molar volume multiplied by the eighth root of viscosity coefficient is a constant (R) called 'rheochor' (cf. parachor).

$$R = (M/d)\eta^{\frac{1}{8}}$$

That is, the rheochor is the molar volume of a liquid at the temperature at which η is unity. The rheochor values have in some cases been found to be additive as also constitutive. Every atom is supposed to have a contribution towards the rheochor of the liquid.

(*ii*) **Dunstan Rule :** Dunstan found a relation between viscosity and molar volume expressed as

$$(d/M)\,\eta \times 10^6 = 40 \sim 60$$

This relationship holds for only normal liquids. Thus for benzene the value is 73 and for acetone 56. But for associated liquids, the value is very high. For glycerine the value is 116400. This rule therefore helps only in finding out if a liquid is normal or not.

(*iii*) **Molecular Viscosity :** The molar surface is $(M/d)^{2/3}$. The product of this surface and viscosity is called molecular viscosity. That is,

$$\text{mol. viscosity} = (M/d)^{2/3}.\eta$$

Thorpe and Rodger showed that at the boiling pt. the mol-viscosity is an additive property. Each atom has a definite contribution towards the molecular viscosity of the liquid. In some cases, this helps in ascertaining the structure of a liquid.

None of these empirical rules are of universal application and are hence rarely employed.

Viscosity and Temperature : Viscosities of liquids decrease with rise in temperature. For most of the liquids the experimental values of log η bear a linear relation with $1/T$, as shown in Fig. (V.10).

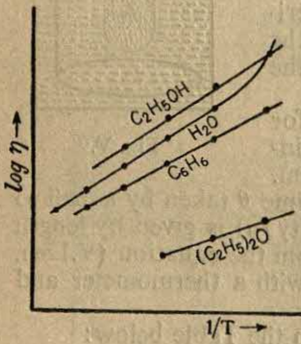


Fig. V.10. log η vs $1/T$

$$\log \eta = \frac{a}{T} + b \qquad \ldots (V.13)$$

where a, b are constants.

The measurement of viscosity has become indispensable in the study of biology and physiology, and also in dealing with various problems of technology, specially in paint, petroleum, ink, colloids, rubber, textiles, etc. The viscosity data are of immense importance in designing chemical engineering equipments, when often gases or liquids are to be pumped. Recently it has been used in determination of mol. wt. of polymers.

Viscosity of Gases : As in the case of liquids, the viscous forces also operate between layers during the steady flow of a gas. The flow of the gas is governed by the Poiseuille's relation (V.10). It should however be remembered that during the flow the mass of gas moves in a definite direction but at the same time the gas molecules have their free random chaotic motion. Considering these motions, it has been shown that the viscosity of a gas may be represented as.

$$\eta_{gas} = \tfrac{1}{3} mnc_a l \qquad \ldots (V.14)$$

where m = mass of a molecule, n = number of molecules/c.c.
c_a = average velocity of molecules, l = mean free path.

Then,

$$\eta_{gas} = \tfrac{1}{3} mn\sqrt{\frac{8kT}{\pi m}} \cdot \frac{1}{\sqrt{2}\pi\sigma^2 n} = \tfrac{2}{3}\frac{\sqrt{mkT}}{(\pi)^{3/2}\sigma^2} \qquad \text{(V.15).}$$

The diameter of a gas molecule is often determined by measuring the viscosity of the gas using the equation (V.15).

The viscosity of a gas is independent of pressure but it decreases with rise in temperature (cf. liquids). The variation of viscosity with temperature for gases is given by

$$\eta = \frac{k_1\sqrt{T}}{1 + C/T} \qquad \ldots \text{(V.16)}$$

where k_1 and C are constants.

Problem : In an Ostwald viscometer, the times of flow of water and alcohol are 80 sec and 175 sec. at 20°C. when their densities are 0.998 and 0.790 gm/c.c. respectively. Viscosity of water at 20°C is 0.01008 poise at 20°C. What is the viscosity of alcohol?

Using eqn. (V.12), $\eta_{alc} = \eta_w . \dfrac{\rho_{alc}.\theta_{alc}}{\rho_w \times \theta_w}$

or $\eta_{alc} = 0.01008 \times \dfrac{0.790 \times 175}{0.998 \times 80} = 0.01747$ poise

EXERCISES

1. Mention the principles which are taken advantage of in liquefying gases. Explain why such steps are necessary.

2. Give an outline of the process of liquefaction of air by Claude's method.

3. What is surface tension? In what units it is expressed? How would you proceed to find out the surface tension of benzene?

4. Explain the terms (*i*) viscosity and (*ii*) coefficient of viscosity. How is viscosity determined by Ostwald viscometer? What is a poise?

5. Discuss the influence of temperature on : (*i*) vapour pressure (*ii*) surface tension and (*iii*) viscosity of liquids.

6. Define parachor. Illustrate its use by an example.

7. Write notes on : (*i*) Trouton's rule (*ii*) Ramsay-Sheilds equation (*iii*) Macleod equation (*iv*) Guldberg rule (*v*) van der Waals forces. (*vi*) Poiseuille's equation

8. Suggest two methods which may be employed to estimate the diameter of the molecules of a gas.

9. How does the viscosities of liquids and gases vary with temperature?

10. Heptane (density 0.7) flows through a viscometer in 63 seconds while the same volume of water requires 108 sec. at 20°C. Calculate the viscosity of heptane if that of water be 0.01005 poise. [Ans. 5.03 millipoise]

11. Water rose to a height of 3.84 cm in a capillary of diameter 0.76 mm. What is the surface tension of water. [Ans. 71.6 dynes cm^{-1}]

12. Equal volumes of water and chloroform flowing through a capillary required 39.7 and 15 seconds respectively. The density of chloroform is 1.49 gm/c.c. and absolute viscosity of water at 20°C is 0.01002 poise. What is the viscosity of chloroform? [Ans. 5.64×10^{-3} poise]

13. The limbs of a vertical U-tube have internal diameters of 1 mm and 0·5 mm respectively. It is partially filled with a liquid of density 0.82 gm/c.c. and surface tension 50 dynes/cm. What is the difference in level of the liquid in the two limbs?

Ans. Using eqn. (V.5b), $$2\gamma\left[\frac{1}{r_1} - \frac{1}{r_2}\right] = \rho . g \Delta h$$

or $$2 \times 50\left[\frac{1}{0.05} - \frac{1}{0.1}\right] = \Delta h \times 0.82 \times 981$$

whence $\Delta h = 1.24$ cm.

14. At 20°C, 10 ml of water gave 29 drops and 10 ml of ether gave 86 drops in the same stalagmometer. The density of ether is 0.7 gm/ml and the surface tension of water is 72 dynes/cm. Calculate the surface tension of ether. (Delhi B.Sc. '77) [Ans. 170 dynes/cm]

15. The sp. heat of vaporisation of toluene is 87·0 cal/gm. at its b. pt. 110·6°C. Using Trouton's rule, estimate its mol. wt. [Ans. 92·6]

16. A steel ball of density 7·99 gm/cc and a diameter of 4 mm requires 53 sec to fall a distance of 1 meter through an oil of density 1·10 gm/cc. Calculate the viscosity of the oil. [Ans. 31·39 poise]

CHAPTER 6

THE SOLID STATE

THE PROPERTIES OF SOLIDS

6.1 Solids

Solids are classified into two groups: (*a*) *Crystalline*, which have a regular shape in the external form together with a regularity in internal arrangement of constituent particles (ions, atoms etc.). They have sharp melting points and have definite planes of cleavage. A crystal is defined as a homogeneous solid bounded by plane faces meeting at fixed angles. Examples, salt, sugar etc. (*b*) *Amorphous*, which show no definite shape and have no sharp melting point. The internal arrangement is not regular. They tend to soften over a fixed range of temperature. They are regarded as supercooled liquids. They have no fixed plane of fracture. Examples, glass, gum, starch etc.

6.2. Polymorphism and Allotropy

Some substances are capable of existing in more than one crystalline form. This phenomenon is known as *polymorphism*. The different crystalline varieties of a substance are called its *polymorphs*. Thus, red and yellow varieties of mercuric iodide are polymorphs. Quartz, flint, opal are the different polymorphic forms of silica. Ammonium chloride, silver nitrate, ice, etc. exhibit polymorphism.

The polymorphism in elements has been given the special name, **Allotropy**. It is the property of an element to exist in different modifications which differ in physical properties and sometimes in chemical properties to some extent. In the allotropism of elements, besides the different crystalline modifications (e.g., S_α and S_β) there may be different atomicity of molecules (e.g. O_2 and O_3).

The different crystalline forms of polymorphs indicate that the internal arrangements of units of the crystals are different. Hence the different polymorphs and different allotropes possess different intrinsic energy. On the basis of stability and energy content, allotropy has been found to be of three types: (*i*) *Enantiotropy* (*ii*) *Monotropy* (*iii*) *Dynamic allotropy*.

(*i*) **Enantiotropy:** Certain allotropes are found to be changed from one form into another with change in temperature. The temperature at which this transformation occurs is called its *Transition temperature*. Above the transition temperature one form is stable and the other form is stable below the transition temperature. At the transition temperature (T_t) both the forms can remain in equilibrium. Examples:

$$\alpha\text{-Sulphur} \quad \overset{96{\cdot}5^\circ\mathrm{C}}{\rightleftharpoons} \quad \beta\text{-Sulphur}$$

$$\text{Grey tin} \quad \overset{13^\circ\mathrm{C}}{\rightleftharpoons} \quad \text{white tin} \overset{202^\circ\mathrm{C}}{\rightleftharpoons} \text{Rhombic tin}$$

Some polymorphous compounds also exhibit enantiotropy.

$$\text{Silver iodide (hexagonal)} \overset{146^\circ\text{C}}{\rightleftharpoons} \text{Silver iodide (regular)}$$

(*ii*) **Monotropy** : In some cases, one allotropic form of an element has a higher energy-content than the other. The form with lower energy content is more stable. In consequence, the form with higher energy has a spontaneous tendency to pass into the stable form. Thus, white phosphorus slowly passes into the red variety which is more stable. The reverse process does not occur normally. Such substances are called *monotropic* substances. One form is always 'metastable' with respect to the other and there is no definite transition temperature.

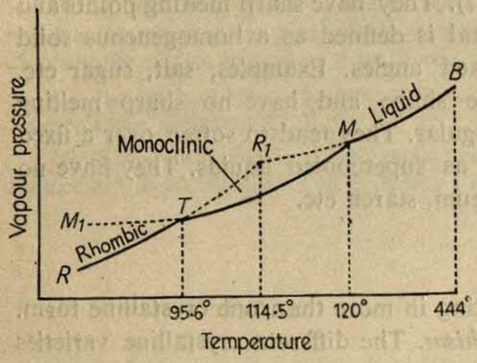


Fig. VI.1a. Enantiotropy: S_α and S_β (not to scale)

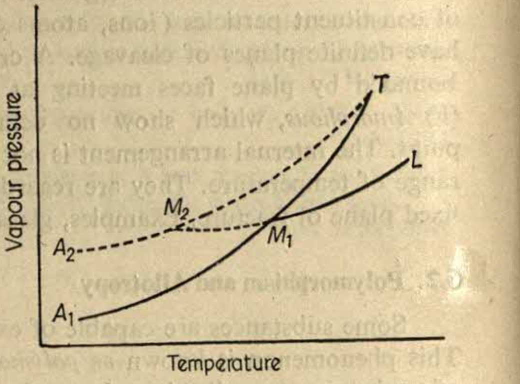


Fig. VI.1b. Monotropy

(*iii*) **Dynamic Allotropy:** Some allotropic forms of an element exist simultaneously at all temperatures. These forms have almost the same energy content. The proportion of the two forms depends upon temperature. There is no transition temperature. This variety is called 'dynamic allotropy'. In liquid sulphur, S_μ and S_λ remain together in equilibrium. Their proportions vary with change in temperature.

Determination of transition temperature : Enantiotropic forms differ in physical properties. At the transition temperature there is an abrupt change in some of the physical properties. The determination of transition temperature is based on the observation of such sudden changes. The most common method of finding out the transition temperature is by *Dilatometric method.*

A dilatometer is used to find out the change in volume of a substance with rise in temperature. It consists of a glass bulb (X) with a capillary elongation (Z) above and a narrow tube (Y) at the bottom. The bulb X is almost filled up with the material under examination through Y and then Y is sealed up. Above the material is kept an inert liquid which fills up a small portion of the capillary as well. At the back of the capillary a scale is fixed. The bulb is then placed in a bath the temperature of which is slowly raised. The level of the liquid will gradually rise. At the transition temperature, the level will suddenly make a sharp change. The transition temperature is noted when this abrupt change occurs. The transition temperature of sulphur can be obtained by this procedure (Fig. VI.1c).

The transition temperature is also often determined from other physical properties, such as from time-temperature curves, from solubility graphs, from measurements of electrode potentials, from vapour-pressure changes, etc.

The transition point and the melting point : (*i*) The transition point is the temperature at which two enantiotropes are in equilibrium; the melting point is the temperature at which the solid phase is in equilibrium with its liquid phase. They are quite similar. (*ii*) Both of them change with pressure in the same way. (*iii*) Both transformations, fusion and transition, are accompanied with thermal changes. (*iv*) The presence of a soluble impurity causes similar changes in both melting point and transition point.

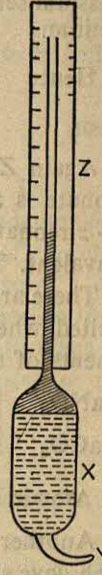


Fig. 1c.
Dilatometer

6.3. Isomorphism

Compounds of similar composition are often found to crystallise in the same form and are said to be isomorphous. Examples:

$KClO_4$	$ZnSO_4,7H_2O$	KH_2PO_4,H_2O	$K_2SO_4,Al_2(SO_4)_3,24H_2O$
$KMnO_4$	$MgSO_4,7H_2O$	KH_2AsO_4,H_2O	$K_2SO_4,Cr_2(SO_4)_3,24H_2O$

Mitscherlich made a careful study of such isomorphous compounds and formulated the principle:

Substances possessing an equal number of atoms united in the same fashion exhibit identity of crystalline forms. It led to the concept that the crystalline form depends upon the number of atoms and the method in which they are united and is independent of their chemical nature. In other words, *substances having similar chemical character and crystalline form should have similar formulae.*

It appears that in isomorphous substances, the atoms substituted must be equal in numbers and should be of same valence and size. This is borne out by the examples cited above. The identity of crystalline form and similarity of formulae are not the only criteria for isomorphism. The following conditions are also to be satisfied:

(*i*) *Formation of mixed crystals* : A solution containing two isomorphous substances on crystallisation will produce homogeneous crystals of the same form containing both the substances in varying proportions.

(*ii*) *Overgrowths* : If a crystal is suspended in a saturated solution of a material with which it is isomorphous, it will grow in size by deposit of the second material retaining the original form. This is mentioned as 'overgrowth'.

It has now been found that isomorphism depends on the ionic or atomic radii. Isomorphism is very common in compounds of transitional elements because their ionic and atomic radii differ only slightly. Equal radii of the substituents in isomorphous compounds help overgrowth as well as formation of mixed crystals.

The law of isomorphism has been used to determine the atomic weight and sometimes to confirm the valence of an element. This is illustrated below:

Mitscherlich found that the chemically similar potassium sulphate and potassium selenate are isomorphous. It was therefore assumed that the formula of potassium selenate would be K_2SeO_4. On analysis it was found to contain 35.39% selenium.

Hence $$\frac{x \times 100}{x \times 39.1 + x + 4 \times 16} = 35.79$$

or atomic wt. of selenium, $x = 79.2$

Again Zirconium was formerly regarded as trivalent. But potassium fluozirconate is found to be isomorphous with K_2SiF_6 and K_2SnF_6. Hence, the fluo- zirconate should be K_2ZrF_6 *i.e.*, zirconium like tin and silicon must be tetravalent. This has since been confirmed.

There are however some exceptions to the law of isomorphism. Instances can be cited where isomorphous substances contain unequal number of atoms or elements of different valence, e.g.,

$NaNO_3$	$KClO_4$	KIO_4	Ag_2S	K_2SO_4, $Al_2(SO_4)_3$, $24H_2O$
$CaCO_3$	$BaSO_4$	$CaWO_4$	PbS	$(NH_4)_2SO_4$, $Al_2(SO_4)_3$, $24H_2O$

6.4. Atomic Heat

Another important property of solids is their heat-capacity, the study of which gave some interesting results.

Dulong and Petit's Law. In 1819, Dulong and Petit suggested from experimental data that *the atomic heat of all solid elements is a constant quantity and is approximately equal to* 6.4 *cal.* Atomic heat is the product of the specific heat of the element and its atomic weight. Hence, specific heat × atomic wt. = 6.4 (approx.). The law holds for many solid elements as shown in Table A.

TABLE A : ATOMIC HEATS

Cu = 6.0	Sn = 6.4	Hg = 6.6
Ag = 6.2	Pb = 6.4	Cd = 6.1
Au = 6.2	Fe = 6.6	Zn = 6.0
Al = 5.8	Ni = 6.4	I = 6.6

This relation along with the knowledge of specific heat enables one to have an idea of the approximate atomic weight of a solid element.

Neverthless, as given in Table B, the Dulong and Petit's Law fails completely in serveral cases of elements with very high m.pt. and relatively low at. wt.

TABLE B : ATOMIC HEATS

Temp.	*Diamond*	*Graphite*	*Silicon*	*Beryllium*	*Boron*
10°C	1.35	1.92	4.6	3.4	3.32
200°C	3.2	3.4	5.6	4.9	—

A classical derivation of the law of Dulong and Petit had been proposed. In the crystal lattice, the atoms have only vibratory motion, the translational and rotational motions are absent. The vibration may occur in three directions and each mode of vibration has two degrees of freedom, each associated with energy, $\frac{1}{2}kT$. In a gm-atom there are N_0 atoms (Avogadro number) present. So the total energy of a gm-atom of solid is given by

$$E = N_0 \times 3 \times 2 \times \tfrac{1}{2}kT = 3RT \qquad \ldots \text{(VI.1)}$$

The heat-capacity at constant volume is the increase in E per degree rise in temperature. Hence, the heat-capacity (C_V),

$$C_V = \left(\frac{\partial E}{\partial T}\right)_V = 3R \approx 6.0 \text{ cal} \qquad \ldots \text{(VI.2)}$$

This is practically the value required by the Dulong and Petit Law. The classical theory however predicts that the atomic heat-capacity should be independent of temperature. But in fact, there is observed considerable variation of the atomic heat with temperature particularly at the lower ranges of temperature. Dulong and Petit's Law fails at low temperature. A very appropriate explanation for the atomic-heat values of solid elements and their variation with temperature has been given by Einstein and by Debye from quantum principles. But those are much involved to be introduced into this text.

CRYSTAL STRUCTURE

6.5. Crystal Systems

Crystals are bounded by plane surfaces, called faces, arranged on a definite plan. The faces reflect the pattern of internal arrangement of ions, atoms, etc. The faces intersect in straight lines called *edges* and the angles formed at the intersection of faces are *interfacial angles*. The crystals of a given substance may vary in size or outward shape, but the *corresponding interfacial angles would always be the same* (Fig. VI. 2). This is often mentioned as the **Steno's Law** of the *constancy of interfacial angles.*

The geometry of a crystal and the location of its faces are defined with the help of 3 (or 4) coordinate non-planer axes. These crystallographic axes may be at right angles to one another or be parallel to some suitably chosen edges of the crystal. A face (if necessary extended) will make intercepts on these axes. The intercepts are denoted by a, b, c. If any other face makes intercepts, say x, y, z

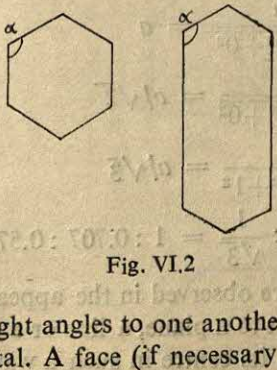


Fig. VI.2

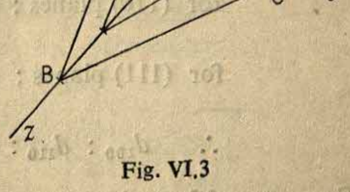


Fig. VI.3

on these axes, then x, y and z will be exact multiples (or exact submultiples) of a, b and c respectively (Fig. VI.3). That is, $x : y : z = pa : qb : rc$ where p, q, r are simple small integers. This is called **Hauy's Law of rational intercepts.**

A given plane is identified or described by taking the reciprocals of coefficients p, q, r. These reciprocals are called **Miller's indices.** The face under consideration has the index, $\left(\frac{1}{p}\,\frac{1}{q}\,\frac{1}{r}\right)$ plane. To wit, suppose the face (ABC) makes intercepts of $2a$, $2b$ and $3c$ (Fig. VI.3). Then its Miller's indices would be $\frac{1}{2} : \frac{1}{2} : \frac{1}{3}$ or $3 : 3 : 2$; the face (ABC) is described as (332) plane. If the face be parallel to an axis, its Miller index would be zero with respect to the said axis. Fig. VI.4 represent some faces by Miller indices.

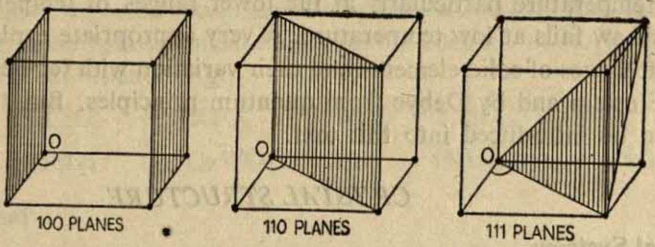


Fig. VI. 4. The faces or planes in a simple cubic crystal

The angles between the chosen axes are denoted by α, β, γ. In the case of the cubic crystals above $\alpha = \beta = \gamma = 90°$.

The distance between parallel planes in a crystal are denoted by d_{hkl}. In the cubic crystal, the interplanar spacings are given by

$$d_{hkl} = \frac{a}{\sqrt{h^2+k^2+l^2}}$$

where h, k, and l are the Miller indices of the plane and 'a' is the value of unit distance along the axis.

Example : Find out the spacings of the three planes (100), (110) and (111) in a simple cubic lattice (Fig. VI.4).

The spacings

$$\text{for (100) planes ; } d_{100} = \frac{a}{\sqrt{1^2+0^2+0^2}} = a$$

$$\text{for (110) planes ; } d_{110} = \frac{a}{\sqrt{1^2+1^2+0^2}} = a/\sqrt{2}$$

$$\text{for (111) planes ; } d_{111} = \frac{a}{\sqrt{1^2+1^2+1^2}} = a/\sqrt{3}$$

$$\therefore \quad d_{100} : d_{110} : d_{111} = 1 : \frac{1}{\sqrt{2}} : \frac{1}{\sqrt{3}} = 1 : 0.707 : 0.577$$

Symmetry : Most often symmetrical features are observed in the appearance of crystals. Symmetry in crystals may be with respect to a plane, a line or a point. When an imaginary plane bisects a crystal through its centre in such a way that one part is the mirror image of the other, it is called a *plane of symmetry*.

If an imaginary straight line is drawn through the centre of a crystal such that on rotation of the crystal through 360° about this line the crystal appears unchanged twice, thrice, four times or six times, it is called an *axis of symmetry*. The axis may be diagonal, trigonal, etc.

A crystal is said to have a *centre of symmetry* if every face has an identical face at equal distance from the centre.

A cubic crystal has the largest number of elements of symmetry. It has one centre of symmetry, thirteen axes of symmetry and nine planes of symmetry.

Classification of crystals: On the basis of lengths of intercepts on the axes and the axial angles. it has been possible to classify the various crystal forms into seven fundamental *systems*. The crystals belonging to any one system may differ in size, shape, elements of symmetry, etc., but their axial ratios as also the axial angles would always be the same, e.g., an octahedral is a cube with exclusive growth of 111 planes (Fig.VI.5). The characteristics of the seven systems and their structures are given below:

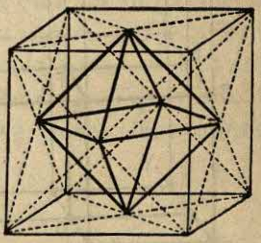
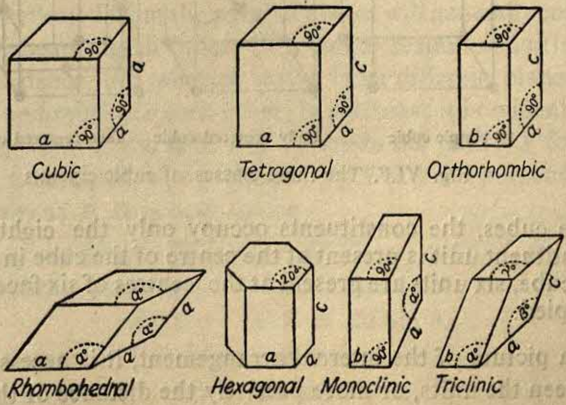


Fig. VI.5
The octahedron

THE SEVEN CRYSTAL SYSTEMS

System		*Axial angles*	*Axial ratios*	*Example*
Cubic	:	$\alpha = \beta = \gamma = 90°$	$a = b = c$	NaCl, Ag, diamond
Tetragonal	:	$\alpha = \beta = \gamma = 90°$	$a = b \neq c$	Sn, SnO_2
Orthorhombic	:	$\alpha = \beta = \gamma = 90°$	$a \neq b \neq c$	$BaSO_4$, KNO_3
Monoclinic	:	$\alpha = \gamma = 90°, \beta \neq 90°$	$a \neq b \neq c$	Gypsum
Rhombohedral	:	$\alpha = \beta = \gamma \neq 90°$	$a = b = c$	$NaNO_3$, ice, Sb
Hexagonal	:	$\alpha = \beta = 90°, \gamma = 120°$	$a = b \neq c$	Graphite, Quartz, Zn
Triclinic	:	$\alpha \neq \beta \neq \gamma \neq 90°$	$a \neq b \neq c$	$K_2Cr_2O_7$, Blue vitriol

It was realised that microscopic building blocks are the unit cells which add up together repeatedly in three dimensions to give the form of a crystal.



Cubic Tetragonal Orthorhombic

Rhombohedral Hexagonal Monoclinic Triclinic

Fig. VI.6. The seven crystal systems

6.6. Space lattice and unit cells

The space lattice is a three-dimensional arrangement of points in which each point has exactly the same environment as its neighbours. Every crystal has such a lattice in which the points are replaced by atoms or ions. If parallel lines be drawn through these points, the whole lattice would be divided into an innumerable identical rhombs (Fig. VI.7). The shape and size of the rhombs will depend upon the parallel lines chosen. The net-work of the atoms or ions is characteristic of the system to which it belongs.

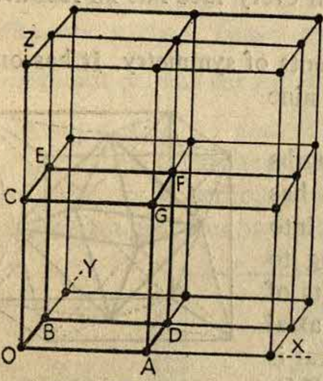


Fig. VI.7. Space lattice

The elments of symmetry and the fact that the form remains the same inspite of increase in size compels one to assume that there should be some elementary blocks which extend in all directions to produce the crystal. This fundamental minute block which by repetition builds up the crystal is the *unit cell.* The unit cell has a content of a minimum number of ions or atoms representing the substance. It is obvious that in such an array in space lattice, there shall be layers or sheets of constituent units (atoms, ions). These layers form the lattice planes and would correspond to the faces of a crystal.

When the discrete arrangement of atoms, ions etc. is taken into account, there arise more than one possible symmetrical arrangement. In other words, for a given system there may be more than one class of crystalline form. The cubic system is the easiest to visualise. In a cubic system, there may be three types of arrangement, namely, simple cube, body-centred cube and face-centred cube, as shown in Fig. VI.8.

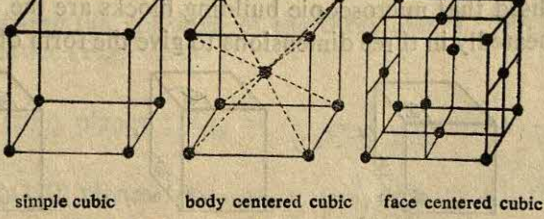

simple cubic body centered cubic face centered cubic

Fig. VI.8. The three classes of cubic crystals

In simple cubes, the constituents occupy only the eight corners. In *b. c.* cube one constituent unit is present at the centre of the cube in addition to corner-units. In f. c. cube, six units are present at the centres of six faces and eight corners are also occupied.

To gain a picture of the internal arrangement, it is necessary to find out the distance between the units, or more precisely the distance of the lattice-planes. It can be conveniently ascertained by adopting the Braggs method.

6.7. The Bragg method of crystal analysis

The interatomic distance is of the order of 10^{-8} cm and the wavelengths of the X-rays are also about 1Å or 10^{-8} cm. W. H. Bragg and his son W. L. Bragg showed that the lattice-planes can serve as *reflection* grating for X-rays. Any face of a crystal has lattice-planes parallel to itself (Fig. VI.9). These lattice planes would reflect the incident X-rays. Braggs developed a very useful and simple relation between the wave length of the X-rays and the spacing between the lattice-planes.

Consider a beam of monochromatic X-rays incident on a set of parallel and equidistant planes, called Bragg's planes, in the crystal structure. Let d cm be the distance between successive planes and let θ be the glancing angle, *i.e.*, the angle between the direction of the incident beam and the planes. In Fig. VI.10, the parallel lines (aa', bb', cc' . . .) represent the successive planes. Now consider an incident ray, say APQ, which meets two planes at P and Q. A portion of the ray AP will be reflected from P along PB, such that the angle BPa' will also be θ. Part of this ray will penetrate and will be reflected from inner planes bb', cc', . . . The reflection of this ray from the second plane bb' occurs at Q in the direction QC, PB and QC being parallel. Draw the line QO perpendicular to the planes at Q meeting the first plane aa' at O. And also draw XOY perpendicular to PB and QC meeting them at X and Y; XOY represents the wave-front of the reflected beam.

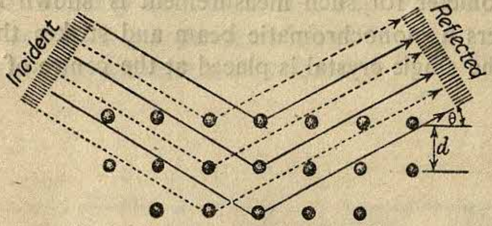


Fig. VI.9. X-rays diffracted from lattice planes

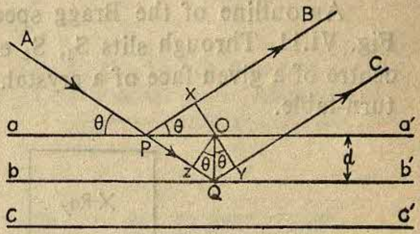


Fig. VI.10. Reflection of X-rays from lattice-planes (Bragg's law)

The beams reflected from the parallel planes will generally combine in different phases and will destroy each other. Only under certain conditions of wavelength and angle of incidence, the reflected waves from different planes will combine in the same phase and reinforce each other. In this case it is evident that constructive interference will occur if the path PQY exceeds the path PX for waves scattered at P by an integral multiple of wavelength (λ). Draw OZ perpendicular to PQ and meeting the latter at Z. It is easy to see,

$$PX = PZ, \text{ and } \angle QOZ = \angle QOY = \theta$$

Hence the excess path, ($PQY-PX$) is equal to

$$ZQY = 2QY = 2d \operatorname{Sin} \theta.$$

This, for constructive interference, must equal $n\lambda$, *i.e.*,

$$n\lambda = 2d \operatorname{Sin} \theta \qquad \ldots \text{(VI.3)}$$

where n is an integer 1, 2, 3, . . . etc. known as the order of reflection.

This is the famous *Bragg equation*, correlating the wavelength of the radiation with the spacing of the lattice-planes.

Now there will be innumerable planes even in a small thickness of the crystal (say more than a million planes per mm thickness). Practically complete interference occurs unless this condition with monochromatic radiation (eqn. VI.3) is satisfied. As 'θ' is changed, strong reflection flash out each time the equation holds with successive values of $n = 1, 2, 3, \ldots$ At other intermediate values of θ, the intensity becomes negligible.

Confining our attention to the 1st order reflection only, *i.e.* ($n = 1$),

$$d = \lambda/2\text{Sin}\ \theta \qquad \ldots(\text{VI.4})$$

The knowledge of θ where reinforcement occurs would enable evaluation of 'd'.

An outline of the Bragg spectrometer for such measurement is shown in Fig. VI.11. Through slits S_1, S_2 enters a monochromatic beam and strikes the centre of a given face of a crystal. The single crystal is placed at the centre of a turn-table.

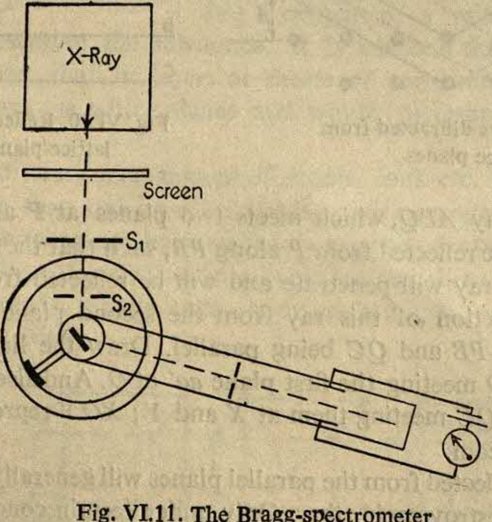


Fig. VI.11. The Bragg-spectrometer

Co-axially with the table and the crystal is a rotating arm carrying an ionisation chamber. Both the turn-table and the arm are provided with circular scales so that the angles through which they are turned can be directly obtained. The ionisation chamber is placed in such a way that the reflected rays from the face of the crystal directly pass into the chamber. The crystal table and the chamber are so adjusted that when the crystal rotates through any angle, the chamber will move through twice that angle. The ionisation chamber is filled with SO_2-gas or methyl bromide vapour and the extent of ionisation is measured with the help of an electrometer connected with it. As the glancing angle (θ) is changed by turning the crystal face slowly, the strength of ionisation is recorded from the electrometer. These are plotted (θ *vs* I) and the maxima are obtained from the graph. The method was first successfully employed by the Braggs in the study of sodium and potassium chloride crystals.

6.8. The crystal structure of Sodium Chloride

Sodium chloride crystal belongs to the cubic systems. Braggs analysed the details of its internal structure by the X-ray method described above. They studied the reflections of monochromatic X-ray beams for 100, 110 and 111 lattice planes of the crystal. The inter-layer distance (*d*) of these three faces for simple cubic, body-centred cubic and face-centred cubic forms could be calculated from geometrical models. The interplanar spacings can be easily conceived from Fig. VI.12a. The calculated spacings of the three types of lattice planes are as follows:

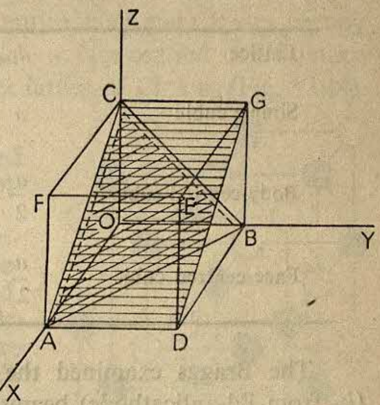
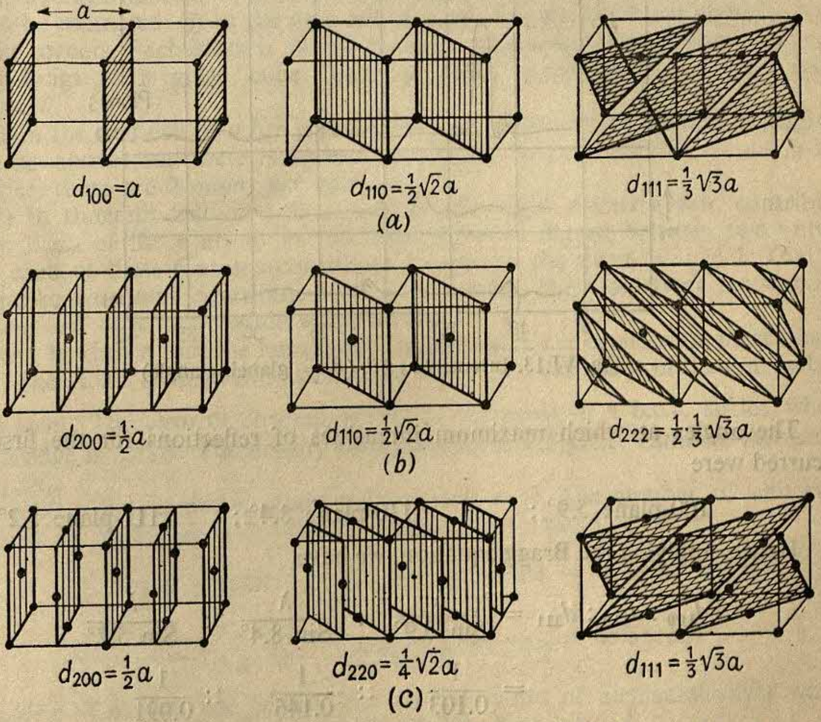


Fig. VI.12. Lattice planes of a cube (ADEF is 100 plane ; ADGC is 110 plane and ABC is 111 plane)



$d_{100}=a$ $d_{110}=\frac{1}{2}\sqrt{2}a$ $d_{111}=\frac{1}{3}\sqrt{3}a$

(*a*)

$d_{200}=\frac{1}{2}a$ $d_{110}=\frac{1}{2}\sqrt{2}a$ $d_{222}=\frac{1}{2}\cdot\frac{1}{3}\sqrt{3}a$

(*b*)

$d_{200}=\frac{1}{2}a$ $d_{220}=\frac{1}{4}\sqrt{2}a$ $d_{111}=\frac{1}{3}\sqrt{3}a$

(*c*)

Fig. VI.12a. Spacings in cubic lattice: (*a*) Simple, (*b*) body-centred and (*c*) face-centred cubic

TABLE : THE CALCULATED SPACINGS OF DIFFERENT LATTICE-PLANES

(a = side of the cube)

Lattice	$d_{100} : d_{110} : d_{111}$
Simple cubic	$a : \frac{a}{\sqrt{2}} : \frac{a}{\sqrt{3}} = 1 : 0.707 : 0577$
Body-centred cubic	$\frac{a}{2} : \frac{a\sqrt{2}}{2} : \frac{a}{2\sqrt{3}} = 1 : 1.414 : 0.577$
Face-centred cubic	$\frac{a}{2} : \frac{a}{2\sqrt{2}} : \frac{a}{\sqrt{3}} = 1 : 0.707 : 1.154$

The Braggs examined the maximum reflections of monochromatic X-ray (k_a from Pd-anticathode) beams from the NaCl-cube surface (100-planes) as also from planes at right-angle to the face-diagonal (110) and from planes perpendicular to cube-diagonals. The intensities of reflections were plotted against the glancing angles of the beams as shown in Fig. VI.13.

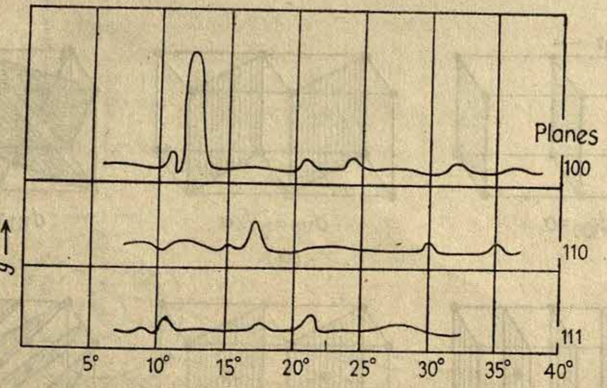


Fig. VI.13. Intensity *vs* 2θ, (θ = glancing angle)

The angles at which maximum intensities of reflections for the first order occurred were

100-plane 5.9° ; 110-plane 8.4° ; 111-plane 5.2°

Hence, applying the Bragg equation, we have

$$d_{100} : d_{110} : d_{111} = \frac{\lambda}{\text{Sin } 5.9^\circ} : \frac{\lambda}{\text{Sin } 8.4^\circ} : \frac{\lambda}{\text{Sin } 5.2^\circ}$$

$$= \frac{1}{0.103} : \frac{1}{0.146} : \frac{1}{0.091}$$

$$= 1 : 0.705 : 1.14$$

Comparing with the calculated values, it is obvious that the sodium chloride crystals must be face-centred cubic type. From the study of relative intensities of reflected beams of different orders and from other relavant considerations, it has been established that in the face-centred cubic lattice, Na^+ and Cl^-ions occupy alternate lattice points in every direction. In fact, a face-centred cubic lattice of Na^+ ions has interpenetrated a face-centred cubic lattice of Cl^-ions (Fig. VI.14).

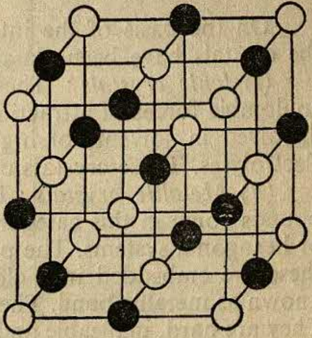


Fig. VI.14. Face-centred cubic lattice of NaCl

X-ray crystallography has been extensively used to reveal the configurations also of giant bio-molecules, interstitial compounds, alloys etc.

There are also other methods for the determination of crystal structures such as Laue's diffraction method, Debye and Scherrer's powder method, electron diffraction and neutron diffraction methods.

The number of atoms or particles which are in the immediate or nearest vicinity to each particle in the crystal lattice is called the co-ordination number of that lattice. An inspection of Fig. VI.8. will reveal that the co-ordination numbers of simple, body-centred and face-centred cubic lattice are 6, 8 and 12 respectively.

The average number of atoms distributed in a unit cell of the cubic lattice can also be estimated. (i) In the unit cell of a *simple cube*, there are eight atoms at the eight corners. Each atom is shared by eight adjoining cubes. Hence $\frac{1}{8}$ of each atom belongs to a given cube. That is, there would be $8 \times \frac{1}{8} = 1$ *atom per unit cell.*

(*ii*) In the unit cell of *a bcc crystal*, the eight atoms at the corners contribute 1 atom (as above) and there is 1 atom completely within the cube. Hence in the *bcc* lattice, there are 2 *atoms per unit cell.*

(*iii*) In the unit cell of *a f.c.c. lattice*, the eight corner-atoms contribute 1 atom. Each of the 6 atoms at the face-centres is shared between two cubes. Hence, each of these 6 atoms contribute $\frac{1}{2}$ atom to the given unit cell. That is, these face-centre atoms contribute $\frac{1}{2} \times 6 = 3$ atoms. Therefore there are 4 *atoms in the unit cell* of a face-centred cubic lattice.

It can be shown that the hexagonal crystals and f.c.c. crystals are most closely packed. The atoms in these two cases occupy 74.1 % of the space in the unit cells.

Problem : The element chromium ($M = 52$) exists in a b.c.c. lattice whose unit cell edge is 2.88Å. The density of chromium is 7.2 g/c.c. Estimate Avogadro number, N_0.

In a b.c.c. lattice, no. of atoms per unit cell = 2. The number of unit cells in 1 mole = $N_0/2$. Let ϕ = volume of unit cell = $(2.88 \times 10^{-8})^3$

$$\therefore \text{ molar volume} = \frac{N_0\phi}{2}, \text{ and gm-mole} = \frac{N_0\phi \times d}{2} = 52$$

$$\text{Or} \quad N_0 = \frac{2 \times 52}{\phi \times d} = \frac{104}{(2.88 \times 10^{-8})^3 \times 7.2} = 6.05 \times 10^{23}$$

Problem : Calculate the density and atomic radius of elemental silver which crystallises in a f.c. cubic lattice with unit cell-length of 4.086 Å.

(*a*) Simple face-centred cubic lattice contains four atoms. Hence density,

$$\rho = \frac{M}{v_m} = \frac{4 \times 107.88}{N_0 \times v} = \frac{4 \times 107.88}{6.02 \times 10^{23} \times (4.086 \times 10^{-8})^3}$$
$$= 10.5 \text{ gm/c.c.}$$

(*b*) The length of face diagonal $= \sqrt{2a^2} = \sqrt{2 \times (4.086\text{Å})^2} = 5.78$ Å

Hence interatomic distance $= \frac{1}{2}(5.78)$ Å $= 2.89$Å; or radius $r = 1.45$Å.

6.9. Bond-types in crystals

On the basis of the internal features and the nature of the building units, the crystals have been classified into the following groups.

(*i*) *Ionic crystals* : These consist of ions held in their lattice positions by coulombic forces of attraction. Salts, such as Na^+Cl^-, are the best examples. When dissolved in solvents of high dielectric constant, they easily separate and form electrolytes. These crystals usually have high melting points.

(*ii*) *Metallic crystals* : The crystals of metals, alloys or intermetallic compounds come in this category. These occur as close-packed systems—either cubic or hexagonal systems. The positive ions of the metal occupy the lattice points and these are embedded in a cloud of electrons. Such arrangement has come to be known as metallic bond. These crystals are good thermal and electrical conductors. They are hard, malleable and ductile, and opaque to light. The easy mobility of the free electrons is responsible for the electrical conductivity of metals. Metals are often lustrous because by absorbing the incident light, the surface electrons are excited. But being free to oscillate, they revert to the original state giving off the energy which seems to have reflected from the surface.

(*iii*) *Covalent crystals* : The building units of these crystals may belong to three types:

(*a*) *Molecular crystals* : The building units are covalent molecules, such as diatomic molecules of H_2, Cl_2, N_2 etc.; organic compounds like benzene, naphthalene, paraffins etc. They are held together by weak van der Waals' forces, non-conductor of heat and electricity, soft and they have low melting points.

(*b*) *Giant layer molecules* like graphite. They form layers of covalently linked atoms. They have high melting points because of their size. One form of boron nitride has such a structure.

(*c*) *Giant three-dimensional structures* : Diamond, quartz, one form of boron nitride belong to this category. The building units are bound by primary bonds and the whole crystal seems to be a giant molecule. They are very hard solids with no malleability and have high melting points.

Crystals of diamond and graphite :

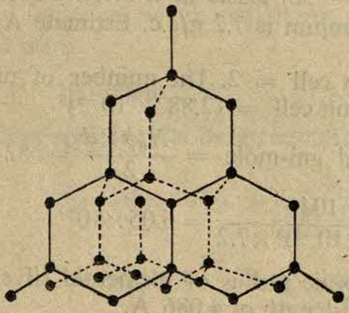


Fig. VI.15. Lattice of diamond

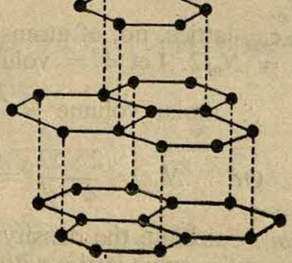


Fig. VI.16. Lattice of graphite

In diamond, the atoms are tetrahedrally united with four other atoms. The interatomic distance is 1.54Å. Graphite is a net-work of hexagonal units in parallel planes. The C-C distance in the hexagon is 1.42Å. The parallel layers are separated by 3.34Å.

EXERCISES

1. Explain, with illustrations, the terms (*i*) allotropy and (*ii*) polymorphism. What different types of allotropy occur and what are the differences between them?

2. Give an outline of a method for the determination of transition temperature of sulphur.

3. What is isomorphism? Discuss the law of isomorphism and its applications. Is the law universally applicable?

4. Define 'atomic heat' of solids. How is Dulong & Petit's law interpreted?

5. Sketch the different possible types of crystals belonging to cubic system. What are the characteristics of a crystal of cubic system?

6. (a) What features distinguish crystalline from amorphous solids ? (b) What is a unit cell ?

7. How is interfacial spacing obtained from X-ray reflection by Bragg's method?

8. Give an outline of the method for the determination of crystal structure of sodium chloride.

9. Write explanatory notes on: (*i*) Space-lattice and unit cells (*ii*) Bragg's equation (*iii*) Miller indices.

10. Name and explain the different bond-types present in crystals. Give examples.

11. Give brief accounts of : (*a*) enantiotropy and transition temperature (*b*) criteria of iscmorphism (*c*) structures of diamond and graphite (*d*) transition point and melting points of solids.

12. How many atoms are present per unit cell of (*i*) a silver crystal which has a f.c.c. structure and (*ii*) an argon crystal having b.c.c. lattice?

13. Silver crystallises in f.c.c. form. The nearest neighbour of Ag-atoms in the crystal are 2.87×10^{-10} m apart. Show that the density of silver is 10.7 gm/c.c.

14. What will be the distance between 110 planes in a simple cubic crystal with a lattice side of 1.5Å? (C.U. '72) [Ans. 1.06Å]

15. Derive Bragg's equation for diffraction of X-rays by crystal lattice. How is this equation utilised to determine crystal structure? (Nagpur '72)

16. In an experiment using X-rays of $\lambda = 2.54$Å, the first order reflection was found to be 30°. Show that the interplanar distance of the face would be 2.54Å.

17. At -190°C argon (at wt. 40) crystallises in f.c.c. form with an edge of unit length 5.4Å. Its density is 1.7 gm/c.c. Calculate Avogadro number.

18. Sodium crystallises in b.c.c. lattice with the unit cube of the side length 4.30A. Show that the density of the metal is 0.96 gm/c.c.

CHAPTER 7

A FEW PHYSICO CHEMICAL PROPERTIES

There are many physical properties of substances the study of which helps the chemists to get an insight of the structure of molecules. A few of these properties will be briefly considered in this chapter.

7.1. Molar Volumes of Liquids : Kopp's Law

The molar volume is generally determined by measuring the density (*d*) and dividing the mol. wt. by the density. From a series of observations, Kopp found that *the molar volume of liquid determined at its boiling point is approximately equal to the sum of the volumes of its atomic constituents.* This is known as *Kopp's Law.*

It implies that the molar volumes in a homologous series should increase by a constant amount as the number of CH_2 groups increase. This is found to be so.

MOLAR VOLUMES OF LIQUIDS

Homologues	*mol. volume*	ΔV_M	*Homologues*	V_M	ΔV_M
C_2H_6	56.7	—	CH_3CH_2OH	57.1	—
C_3H_8	74.6	17.9	$CH_3CH_2CH_2OH$	73.4	16.3
C_4H_{10}	96.0	21.4	$CH_3(CH_2)_2CH_2OH$	89.9	16.5
C_5H_{12}	117.8	21.8	$CH_3(CH_2)_3CH_2OH$	106.1	16.2
C_6H_{14}	139.9	22.1	$CH_3(CH_2)_4CH_2OH$	122.5	16.4
C_7H_{16}	162.5	22.6	$CH_3(CH_2)_5CH_2OH$	138.7	16.2

From the study of a large number of compounds, the different atoms were given values for their atomic volumes. The values accepted now are :

atom	:	C	H	Cl	S	O(carbonyl)	O (ester)
At. volume	:	14.8	3.7	22.2	25.6	7.4	11.0

atom	:	O (acid)	N	N_{amine} prim	N_{amine} Sec.	benzene ring
At. volume	:	12.0	15.6	10.5	12.0	−15.0

These values show that molar volume is also constitutive to some extent. The atomic volume of oxygen or nitrogen would be different if present in different functional groups.

The isomers in the same family have the same molar volumes. But if the isomers belong to different families the molar volumes would be different. The Table below would show.

MOLAR VOLUMES OF LIQUIDS

Isomers	V_M = *mol. volume*	*Isomers*	V_M = *mol. volume*
n-heptane	162.6	Acetone	77.2
Isoheptane	162.2	Propyl aldehyde	75.4
Butyric acid	108.2	Methyl propyl ether	105.1
Isobutyric acid	108.9	Butyl alcohol	101.9
Propyl alcohol	81.2	Ethyl benzoate	174.6
Isopropyl alcohol	81.8	Phenyl propionic acid	170.4

Thus, an estimate of the molar volume would help in the detection of constitution of the molecule.

7.2. Optical activity

When a light ray passes through a transperant medium (air, water, glass etc.), its transverse vibrations proceed in all possible planes at right angles to the direction of propagation. But if such ordinary light be allowed to pass through a Nicol prism, the transmitted light is confined to a single plane. The Nicol prism is a specially cut iceland spar (transperant crystalline $CaCO_3$). The transmitted light in one plane is called *polarised light* and the plane of its propagation is called *plane of polarisation.* The plane of polarisation can be identified by placing a second Nicol in the path of the polarised light. If the second Nicol be *in phase* with the first then light would pass through it. But if the second Nicol be not parallel to the first for its optical planes, then most of the light would be cut off.

There are substances, such as lactic acid, glucose solution, etc. which when placed in the beam of polarised light, the plane of polarisation is rotated either to the right or to the left. These substances are called *optically active* substances. Those which turn the polarised light towards the right are *dextro-rotatory* and those which turn it towards the left are *laevo-rotatory.*

The extent of rotation is measured by an instrument called 'polarimeter', which essentially consists of two Nicol prisms, co-axially placed (Fig. VII.1). The first one, called *polariser*, through which a monochromatic beam is introduced is kept fixed. The second Nicol prism, called *analyser*, is mounted on a rotating

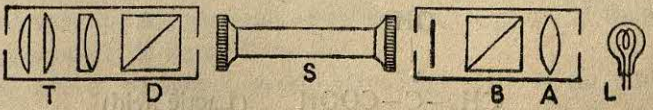


Fig. VII.1. Arrangement in a polarimeter. [L, light source; A, lens; B, polariser; S, tube containing liquid ; D, analyser ; T, telescope.]

disc. The plane polarised light emerging from the first prism (B) falls on the second (D). If the second prism be at 90° to the polariser, a complete darkness would occur, when viewed through a telescope (T) placed on the other side of the analyser. Initially the instrument is so adjusted that the entire field of view looked through the eye-piece would have uniform brightness. The polarimeter is set at this position, and the reading of the position is taken.

The liquid or the solution whose optical activity is to be measured is then taken in a tube of fixed length (usually 10 cm or 20 cm) and placed in between the polariser and the analyser and co-axially with them. The liquid turns the plane of polarised beams and as such the field of view will be illuminated now non-uniformly, as seen through the telescope. The analyser is now rotated till the field becomes one of uniform illumination as before. The new position is read from the scale. The difference of the two readings is the angle through which the polarised beam has been rotated by the liquid or the solution. Thus we can ascertain the optical activity of the substance.

The magnitude of rotation depends upon several factors: (*i*) the density or concentration of the substance, (*ii*) the temperature, (*iii*) the wavelength of the light and (*iv*) the length of the substance through which the beam has to pass.

The rotatory power of the substance is expressed in terms of specific rotation, $[\alpha]_\lambda^t$ such that

$$\left[\alpha\right]_\lambda^t = \frac{\alpha}{l.d} \qquad \ldots(\text{VII.1})$$

where α is the observed rotation of polarised beam at t°C caused by l-decimeter of liquid (density, d). λ is the wavelength of light used.

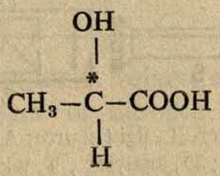
In the case of a solution of conc. c expressed in gm per cc.

$$\left[\alpha\right]_\lambda^t = \frac{\alpha}{l.c} \qquad \ldots(\text{VII.2})$$

The specific rotation is thus the rotation produced by a solution containing 1 gm of the substance per c.c. when the length of the column through which the light passes is 10 cm. The specific rotation is a characteristic property of the optically active species. The molar rotation has been defined as

$$\left[\alpha_M\right]_\lambda^t = \frac{M}{100}\left[\alpha\right]_\lambda^t \qquad \ldots(\text{VII.3})$$

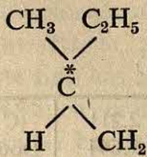
Optical rotation and chemical constitution : Van't Hoff and Le Bel independently pointed out the connection between the optical activity and the asymmetry present in the molecule of the substance (1874). Most of the optically active substances are organic compounds whose molecules contain at least one carbon atom having its four valences satisfied with four different radicals or atoms. Such a carbon atom is called an asymmetric C-atom (marked with asterisk below). The simplest example is lactic acid,



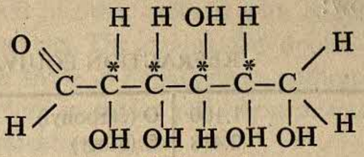
$$CH_3-\overset{\overset{\displaystyle OH}{|}}{\underset{\underset{\displaystyle H}{|}}{\overset{*}{C}}}-COOH$$

(Lactic acid)

Other examples may be cited, *e.g.*,



(Amyl alcohol)



(Glucose)

Thus optical activity of a substance indicates existence of one or more assymmetric C-atoms. In a few cases, structural asymmetry also causes optical activity.

The optically active substances occur as pairs of isomers. One is the *l*-form, *i.e.*, laevo-rotatory and the other is the *d*-form or dextro-rotatory. These are optical isomers. Thus there are the *l*-lactic acid and *d*-lactic acid, or *l*-tartaric acid and *d*-tartaric acid. Structurally one is the exact non-superimposable mirror-image of the other. The chemical and plysical properties of the isomers are identical. They differ only in their interaction with polarised light. An equimolar mixture of the two forms is optically inactive and is called the *racemic* (*dl*) variety.

7.3. Molar Refraction

In 1980, starting from Maxwell's electromagnetic theory of light, Lorenz and Lorentz independently deduced a relation between density (d) and refractive index (n) of a substance expressed in the form,

$$\frac{n^2-1}{n^2+2}\cdot\frac{1}{d} = R_s$$

R_s is called the *specific refraction* of the substance and is independent of temperature. Moreover the specific refraction has also been found to be almost the same both for the liquid and the gaseous state of the substance.

Multiplying both sides of this relation by the mol. wt. M of the substance, we obtain the *molar refraction*, R_M;

$$R_M = M \times R_s = \frac{n^2-1}{n^2+2}\cdot\frac{M}{d} \qquad \text{. . . (VII.4)}$$

Since the refractive index n, being a ratio of velocities, is a dimensionless quantity, the molar refraction R_M has units of volume and is usually expressed in c.cm per mole. The refractive index is often accurately determined with the help of a Pulfrich or an immersion refractometer.

The molar refraction is partly additive and partly constitutive. When the molar refractions of successive members of a homologous series are measured, the increase in the value of R_M for each addition of CH_2 group is found to be the same, *i.e.*, the property is an additive one.

As in the case of parachors, every constituent atom of the molecule has a contribution to the molar refraction. This contribution may be called 'atomic refraction equivalent'. The presence of double or triple bonds, etc. raises the molar refractivity showing also its constitutive character. The refraction equivalents are given below:

REFRACTION EQUIVALENTS (r_D)

H	1.100	O (carbonyl)	2.211	(C = C) 1.733
C	2.418	O (ether)	1.644	Double bond
Cl	5.967	O (hydroxyl)	1.522	(C ≡ C) 2.398
Br	8.865	N (Primary amines)	2.322	Triple bond
I	13.900	N (Secondary amines)	2.499	
S (sulphides)	7.97	N (Tertiary amines)	2.840	

Calculated from these refraction equivalents (r_D), the molar refractivity R_M for ethyl methyl ketone would be

$$R_M = 4 \times 2.418 + 8 \times 1.10 + 2.211 = 20.683,$$

the experimental value is 20.674. Other examples are:

R_M	*acetic acid*	*acetone*	*chloroform*	*diallyl*	*benzene*
Calc.	12.91	16.07	21.42	28.78	26.31
Obs.	12.93	16.15	21.40	28.77	26.15

This additive property predicts that R_M-values will regularly increase in a homologous series. This has been confirmed.

Series	R_M (D-line)	△	*Series*	R_M (D-line)	△
CH_3OH	8.218		C_6H_{14}	29.878	
C_2H_5OH	12.739	4.521	C_8H_{18}	39.160	2×4.641
C_3H_7OH	17.515	4.676	$C_{10}H_{22}$	48.501	2×4.670
C_4H_9OH	22.130	4.615	$C_{12}H_{26}$	57.845	2×4.672
$C_5H_{11}OH$	26.744	4.614			

Again, of the two isomers, allyl alcohol and propyl aldehyde should have different molar refractivities as the former one has *a* '*c*=*c*' double bond. The results confirm the same ;

allyl alcohol ($CH_2 = CH.CH_2OH$): $R_{M\,\mathrm{calc}} = 17.112$; $R_{M\,\mathrm{obs}} = 16.973$

propyl aldehyde (CH_3CH_2CHO) : $R_{M\,\mathrm{calc}} = 16.065$; $R_{M\,\mathrm{obs}} = 15.970$

Thus determination of R_M-values helps in detecting the difference in constitution in the case of isomeric compounds.

The molar refractivities of liquids having conjugated double bonds in their moles have much higher values than those calculated. Example:

		$M_{R(\alpha)}$	
		obs. :	*calc.*
Diallyl	$CH_2 = CH-CH_2-CH_2-CH = CH_2$,	28.77	28.78
Isodiallyl	$CH_3-CH = CH-CH = CH-CH_3$,	29.87	28.78 (△ = 1.09)

Such discrepancies are also found in other systems with conjugated double bonds such as styrene, acetophenone etc. The conjugated double-bonds in the closed benzene ring has no effect, but those in naphthalene, anthracene, etc. have marked effect. Such anomalous increase in molar refraction due to presence of conjugated double bonds is called **optical exaltation**

7.4. Polar and Non-Polar Molecules : Dipole moment

Molecules are composed of positively charged nuclei and negatively charged electrons distributed in space. The structural arrangement of these particles is different for different molecules. It will be easily conceived that the centre of gravity of the positive nuclei may or may not coincide with that of the negative electrons. When the centre of gravity of the positive charges in a molecule is exactly at the same point as that of the electrons, it is a *non-polar molecule.* Instances of non-polar molecules are found in H_2, Cl_2, N_2, CO_2, CH_4, C_6H_6, etc. On the other hand, in many molecules like those of HCl, CH_3Cl, $CHCl_3$, $C_6H_5NO_2$, H_2O, NH_3, etc. the centres of gravity of the positive and the negative charges do not coincide; such molecules are said to be *polar molecules.*

Since the molecule as a whole is neutral, if we have a total charge $+ e$ at the centre of positive charges, the charge at the centre of negative charges would be $-e$. If l be the distance between the two centres of gravity in a polar molecule, it is said to have a permanent electric moment called the *dipole moment* (μ), given by,

$$\mu = e \times l \qquad \ldots \text{(VI.5)}$$

In a non-polar molecule the distance $l = 0$; so the dipole moment is nil.

The charge of an electron is 4.77×10^{-10} e.s.u. and the distance between the centres is of the order 10^{-8} cm. Hence the dipole moment is of the order of 10^{-18} e.s.u. of moment. It is called a Debye unit: 1 *d* (debye unit) = 10^{-18} esu-cm.

7.5. Molar Polarisation

When molecules are placed in an electric field, say, the parallel plates of a charged condenser, two effects are produced in them.

(*i*) Firstly, the field causes a distortion of the electric charges within. The positive nuclei would be attracted towards the negative plate and the electrons towards the positive plate. As a result the centres of positive and negative charges would shift.

Even if it be a non-polar molecule, there would be an electrical distortion in the molecule, as shown in Fig. VII. 2, to form an electrical *dipole.* Such distortion of the centres of positive and negative charges is called **induced polarisation** (P_i). The distortion would disappear when the field is withdrawn.

If the molecules be polar, a similar distortion or displacement of centres of positive and negative charges would occur and there would also be an induced polarisation (P_i). The induced polarisation is independent of temperature.

(*ii*) The second effect is concerned only with the polar molecules. Each of the polar molecules has a positive and a negative end. The field would tend to orient all the molecules in the direction of the field, the positive ends pointing towards the negative plate. But the thermal agitations would oppose such orientation and the molecules would take up some mean positions between the direction of the field and their original positions as in Fig. VII.3. This effect of the field on the dipoles is called **orientation polarisation** (P_0).

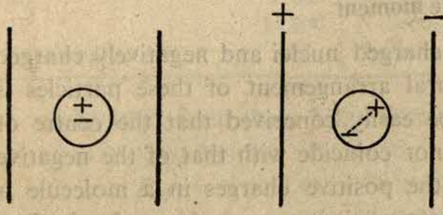


Fig. VII.2. Induced polarisation

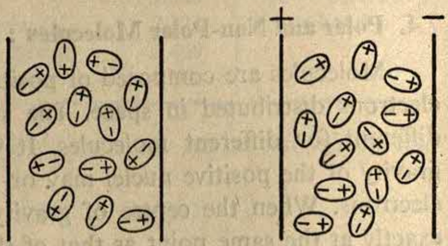


Fig. VII.3. Orientation polarisation

The total *molar polarisation* (P_t) is the sum of the induced and orientation polarisations.

$$P_t = P_i + P_0 \qquad \ldots \text{(VII.6)}$$

In the case of non-polar molecules, $P_0 = 0$.

Mosotti and Clausius worked out an expression for the total molar polarisation, which is an important property of the substance. It is formulated as,

$$P_t = \frac{D-1}{D+2} \cdot \frac{M}{d} \qquad \ldots \text{(VII.7)}$$

where, D, d and M are dielectric constant, density and mol. wt. of the substance. The determination of dielectric constant by any standard physical method gives the value of P_t.

It was Debye who showed that the orientation polarisation (P_0) of polar molecules is given by,

$$P_0 = \tfrac{4}{3}\pi N_0 \left(\frac{\mu^2}{3kT}\right) \qquad \ldots \text{(VII.8)}$$

in which μ = dipole moment, N_0 = Avogadro number and k = Boltzmann constant.

Substituting in equation (VII.6), we have

$$\frac{D-1}{D+2} \cdot \frac{M}{d} = P_i + \tfrac{4}{3}\pi N_0 \left(\frac{\mu^2}{3kT}\right) \qquad \ldots \text{(VII.9)}$$

or

$$P_t = P_i + \frac{4\pi N_0 \mu^2}{9k} \cdot \frac{1}{T}$$

i.e.

$$P_t = P_i + b/T, \qquad \ldots \text{(VII.10)}$$

where

$$b = \frac{4\pi N_0 \mu^2}{9k}$$

Determination of dipole moment : One method for determination of dipole moment (μ) depends on the use of the equation (VII.10). The total polarisation (P_t) is measured at different temperatures. The plots of P_t against $1/T$ always give straight lines (Fig. VII.4) as P_i is independent of temperature.

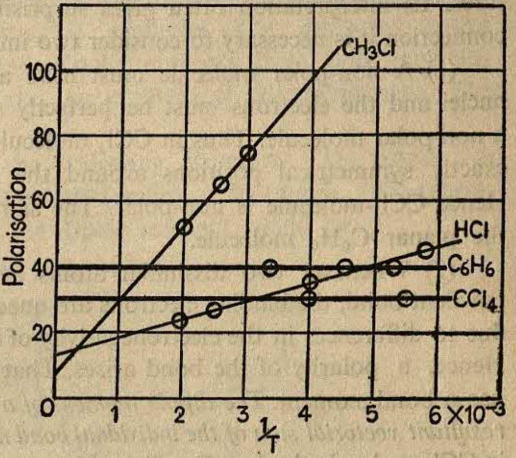


Fig. VII.4

The slope of the line is measured from which 'b' is known.

$$\text{Now} \qquad b = \frac{4\pi N_0}{9k}\mu^2$$

$$\text{or} \qquad \mu = \sqrt{\frac{9k}{4\pi N_0}}.\sqrt{b}$$

$$= 0.0128 \times 10^{-18}\sqrt{b}\ \text{esu-cm}$$

(putting the values of k and N_0). The dipole moment (μ) is thus obtained. When the straight lines are found to be parallel to the $1/T$-axis obviously $b = 0$, i.e. μ is also zero. The molecules such as C_6H_6, CCl_4, etc are non-polar.

The dipole moments of some substances are given below:

Molecules which have a centre of symmetry are non-polar ($\mu = 0$); for example, H_2, N_2, Cl_2, Br_2, O_2 CO_2, CS_2, $SnCl_4$, etc. are non-polar. Similarly, CH_4, C_2H_6, C_2H_4, C_2H_2, C_6H_6, $C_{10}H_8$, CCl_4, CBr_4, etc. are also non-polar, as these molecules have centres of symmetry.

TABLE: DIPOLE MOMENTS OF SOME SUBSTANCES (DEBYE UNITS)

Substance	*Dipole moment*	*Substance*	*Dipole moment*
HCl	1.03	CH_3Cl	1.86
HBr	0.78	CH_3Br	1.80
HI	0.38	CH_3I	1.35
H_2O	1.84	alkyl chlorides	2.03
H_2O_2	2.10	methyl alcohol	1.70
NH_3	1.49	methyl amine	1.24
N_2H_4	1.84	acetic acid	1.74
N_2O	0.17	chlorobenzene	1.73
H_2S	1.10	*p*-dichloro benzene	0.00
HCN	2.90	*m*-dichlorobenzene	1.72
SO_2	1.63	*o*-dichlorobenzene	2.50
CO	0.12	nitrobenzene	4.23
PH_3	0.55	*p*-nitrochlorobenzene	2.83
PCl_3	0.78	*m*-nitrochlorobenzene	3.73
AsH_3	0.16	*o*-nitrochlorobenzene	4.64
$AgClO_4$	4.70	aniline	1.56

7.6. Dipole Moment and Molecular Structure

Dipole moment is a valuable weapon in the determination of molecular structures. Its interpretation often gives surprisingly important informations. In this connection it is necessary to consider two important facts.

(1) A non-polar molecule must have an electrical centre of symmetry. The nuclei and the electrons must be perfectly symmetrically distributed in space in a non-polar molecule. Thus in CCl_4 molecule, the nuclei and the electrons occupy exactly symmetrical positions around the carbon nucleus in the tetrahedron. Hence CCl_4-molecule is non-polar. The same is true of linear CO_2-molecule. or the planar C_6H_6 molecule.

(2) Whenever two dissimilar atoms are linked by a covalent bond, the binding electrons are unequally attracted due to differences in the electronegativity of the two atoms. Hence, a polarity of the bond arises. That is, every bond has a bond moment. *The dipole moment of a molecule is the resultant vectorial sum of the individual bond moments.* Thus, in CCl_4-molecule the four C—Cl bond moments (1.5*d*) are spatially distributed towards the vertices of a tetrahedron. Geometrically, the resultants of these moments neutralise each other. The net moment is zero. It is non-polar. On the other hand, in CH_3Cl-molecule, the bond-moments (C—H 0.4*d*, C—Cl 1.5*d*) on vectorial summation would not be *zero*. Hence it is polar (Fig. VII.5).

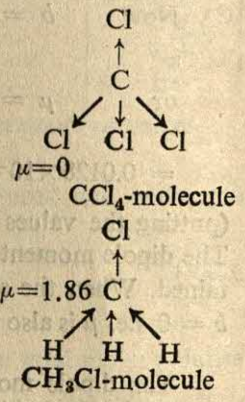


Fig. VII.5

Carbon dioxide has been found to be non-polar ($\mu=0$). With C-atom at the middle, the triatomic molecule may have either the linear structure (I) or the triangular structure (II). In the structure (II), the C—O bond moments would not neutralise one another and the molecule would be polar. On the other hand, in the linear structure (I) , the bond-moments being opposite would cancel one another. As such, the non-polar carbon dioxide molecule must have a linear structure.

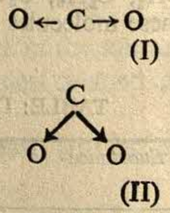


Fig. VII.6

The water molecule (triatomic like CO_2) has a large dipole moment, which rules out the possibility of its having a symmetrical linear structure. The molecule has therefore a triangular structure, the two O—H bonds meeting at an angle.

Benzene is non-polar. It confirms the Kekule structure and that it has a planar configuration with six hydrogen atoms in the same plane. The centre of the regular hexagon is the electrical centre of symmetry. If a part of the hexagon or if the hydrogen atoms were not in the same plane, it is easy to see that the molecule would have been polar.

Similarly, boron trichloride is non-polar which suggests that it has a planar configuration with three chlorine atoms at the corners of an equilateral triangle and boron at the intersection of medians. But PCl_3 or NH_3 molecules have dipole moments. In these molecules, the three halogen or hydrogen atoms are in one plane symmetrically placed in relation to the nitrogen (or phosphorus) atom placed at the apex of a regular pyramid.

That the vector sums of bond-moments lead to the dipole moment of the molecule can be illustrated by innumerable examples. The measured dipole moments and the theoretically computed dipole moments from bond-moments compare very satisfactorily. Let us take the example of dinitrobenzenes. The C$-$NO$_2$ bond moment is 3.9*d*.

The three dinitrobenzenes have the following structures. The angles (θ) between the two substitution groups are 60° (ortho), 120° (meta), 180° (para). If m denotes the bond moment, then the dipole moment would be

$$\mu = [m^2 + m^2 + 2m^2 \operatorname{Cos}\theta]^{\frac{1}{2}}$$

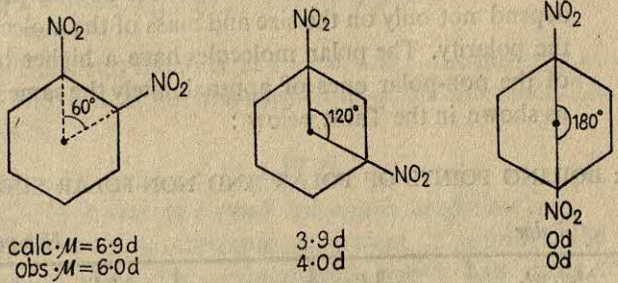


Fig. VII.7. Dipole moments of O$-$, m$-$, p$-$dinitrobenzenes.

The observed and the calculated values of the moments for the three dinitrobenzenes agree well.

	Ortho	Meta	Para
μ (obs.)	6.9	3.9	0 *d*
μ (calc.)	6.0	4.0	0 *d*

To take another example, let us consider the simplest molecule, methane. Its non-polar character is easily understood from its symmetrical tetrahedral structure with the C-atom at the centre and the four identical valences making an angle of 109°28′ with each other. The centre of symmetry is at the nucleus of the C-atom. The absence of dipole moment in the methane molecule implies that any one C-H bond moment exactly counterbalances the net moment contributed (vectorially) by the remaining three C-H bonds *i.e.*, the methyl group as a whole. The CH$_3$-group has a regular pyramidal configuration with C-atom at its apex and three hydrogen at the base (Fig. VII.7a). The resultant moment of the three C-H bonds will be directed along a line from the centre of the base towards the apex and opposite to the fourth C-H bond moment direction. Using symbol *m* for bond moments, the resultant moment of the CH$_3$-group is given by

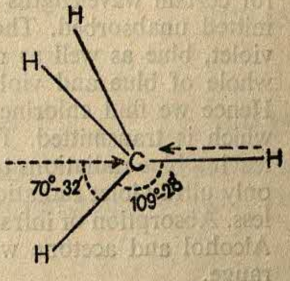


Fig. VII.7a

$$m_{CH_3} = 3m_{CH} \operatorname{Cos}(180° - 109°28') = 3m_{CH} \times \tfrac{1}{3} = m_{CH}$$

That is, the moment of CH_3-group is the same as that of the C-H bond, *i.e.*, 0.4*d*. Again the bond moment for C—Cl link is 1.4*d*. So, the dipole moment of $\overrightarrow{CH_3}-\overrightarrow{Cl}$ would be $0.4 + 1.5 = (1.9d)$, both acting in the same direction. The observed dipole moment for CH_3Cl is 1.86 *d* (Fig. VII.5).

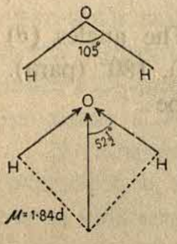


Fig. VII.7b

The measured dipole moment of water is 1.84*d* and it results from two identical OH bonds each of moment 1.6*d*. The resultant as shown in Fig. VII.7b works out to an angle of 105° between the two bonds. This illustrates the application of bond moments and also shows how the dipole moment enables us to determine the bond angles and hence the structure.

It may be mentioned here that the boiling points of liquids depend not only on the size and mass of the molecule but also on the polarity. The polar molecules have a higher b. pt. than that of the non-polar ones of approximately the same molecular mass as shown in the Table below :

TABLE: BOILING POINTS OF POLAR AND NON-POLAR SUBSTANCES

Polar			*Non-polar*		
	Mol. wt.	*B.P.*		*Mol. wt.*	*B.P.*
PH_3	34	−85°C	SiH_4	32	−112°C
AsH_3	78	−55°	GeH_4	77	−90°
SCl_2	103	59°	BCl_3	117	18°
ICl	162	97°	Br_2	160	59°

7.7. Absorption of Light

When light passes through a body, a portion of it may be absorbed. The absorption of light by a substance is selective. A substance has its own preference for certain wavelengths of radiation which it will absorb, the rest would be transmitted unabsorbed. The iodine vapour absorbs strongly in the green, allowing violet, blue as well as red to be transmitted. Similarly, chlorine absorbs almost whole of blue and violet of the white light, and green to red are transmitted. Hence we find chlorine yellowish green. The colour of a substance is the light which is transmitted. The $CuSO_4$ solution is blue for it absorbs yellow to red leaving blue radiations to be transmitted. A substance, like benzene, which absorbs only ultra violet radiations, will transmit all white light and would appear colourless. Absorption of infra-red radiations also takes place and there too it is selective. Alcohol and acetone would absorb different radiations in the infra-red spectral range.

The radiations on being absorbed raise the energy-levels *i.e.* quantum levels of the molecules. (*i*) Absorption in the ultra-violet and visible region raises the electronic quantum level. (*ii*) Near infra-red radiation on absorption increases the vibrational energy level. (*iii*) Absorption of far infra-red radiations raises the rotational energy level.

The amount of radiation absorbed is determined by measuring the intensities of incident and transmitted light by photo-cells. The absorption of radiation is governed by two laws—the Lambert's law and the Beer's Law.

Lambert's Law states that *the rate of decrease of intensity with the thickness of absorbing medium is proportional to the intensity of the penetrating radiation.* Consider a thin layer of the medium of thickness l and let I be the intensity of the radiation entering it, then

$$\frac{dI}{dl} = -kI \quad \text{or} \quad \int_0^I \frac{dI}{I} = -\int_0 kdl$$

$$\text{or} \qquad ln\frac{I}{I_0} = -kl; \;\; i.e., \qquad I = I_0e^{-kl}$$

where I_0 is the (incident) intensity at $l = 0$, and I, the intensity at distance l. The constant k is called the '*absorption coefficient*' of the substance. The equation may also be written as,

$$I = I_0 10^{-al} \qquad \text{...VII.11)}$$

where $a = 0.4343\ k$ and is termed '*extinction coefficient*'.

When the absorbing substance is present in solution, the absorption of light also depends upon the concentration. **Beer's Law** states that *the rate of decrease in intensity of radiation absorbed is proportional to the intensity of radiation and to the concentration of the solute.* Hence, using the same symbols,

$$\frac{dI}{dl} = -k'cI, \qquad \text{(where } c = \text{concentration)}$$

$$\text{or} \qquad \int_{I_0} \frac{dI}{I} = -\int_0^l k'cdl, \quad \text{or} \quad ln\frac{I}{I_0} = -k'cl$$

$$\therefore \qquad \frac{I}{I_0} = e^{-k'cl} \qquad \text{...(VII.12)}$$

$$\text{or} \qquad k' = \frac{1}{cl}ln\frac{I_0}{I}, \qquad \text{...(VII.13)}$$

where k' is called the *molar absorption coefficient.*

Rewriting, $I = I_0\ 10^{-0.4343k'cl} = I_0\ 10^{-\epsilon cl}$ ...(VII.14)

so that ϵ, called the *molar extinction coefficient*, is given by $\epsilon = 0.4343k'$. The value of ϵ is specific for a given substance for a given wavelength of light. The quantity $\log I_0/I$ is called optical density (D), so

$$D = \log I_0/I = \epsilon cl \qquad \text{...(VII.15)}$$

The molar extinction coefficient ϵ varies largely with the wavelength of the light used. When white light passes through a coloured transparent substance and the transmitted light is analysed, it is found that the light is absorbed to a very large extent (sometimes almost wholly) in certain spectral ranges. These ranges are called its absorption bands and are characteristic of the substances used, On either side of the absorption bands, the intensity of light remains practically unreduced, *i.e.* almost the same as the incident intensity. Now-a-days with the help of a *photoelectric spectrophotometer*, the ratio of the intensities of transmitted light (I) and of incident light (I_0) is directly measured. Different monochromatic radiations with continuously increasing wavelengths are led through the substance contained in a cell of constant thickness (l). The values of I/I_0 for lights of different wavelengths are determined. The plot of I/I_0 versus λ gives an irregular curve, the minimum points of these curves indicate the absorption bands. If percentage absorbance log I_0/I be plotted against λ, then the maxima of the curve will correspond to the absorption bands.

Molecules in which double or triple bonds are present give rise to typical absorption bands in *U-V* spectra. Hence occurrence of such a spectra helps us in detecting and identifying unsaturation. Large absorbances are found in molecules with conjugated double-bonds.

7.8. Infra-red absorption

Similar selective absorption bands are also found with infra-red radiations. In an *I-R* spectrometer, a narrow beam of radiations covering a small range of wavelength in the *I-R.* region is led through the substance or its solution. The percentage of transmittance is recorded by a photometer. The percentage absorbance is then plotted against $\bar{v}$ (wave number). The maxima of the curves indicate absorption bands. Different functional groups produce easily recognisable band at nearly definite positions of the spectral range. Such spectra are hence often characterised as 'molecular finger-prints' which detect the presence of functional groups. To illustrate: A C=O group usually produces a peak at 1700 cm^{-1}. It will be evident from Fig. VII. 8, in which infra-red spectrograms of benzaldehyde and phenyl-methyl ketone are shown. The pronounced peaks near 1700 cm^{-1} are indicative of the pressence of the CO-group in both the compounds. The three absorption peaks near 1600 cm^{-1} are indicative of the aromatic nucleus

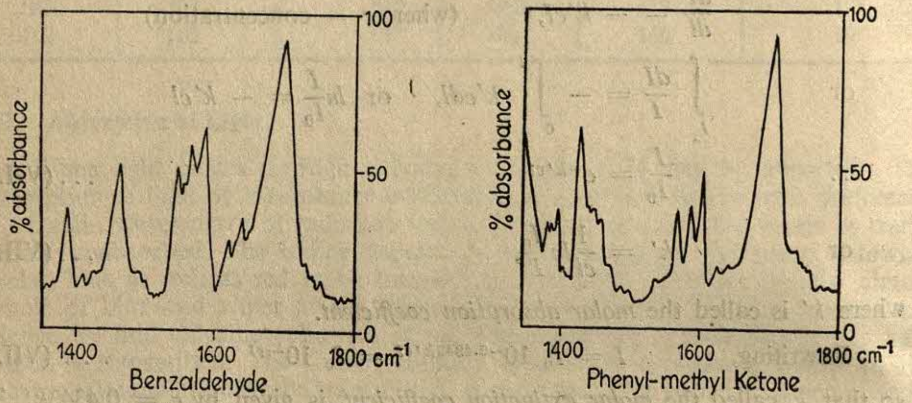


Fig. VII. 8: I.R. spectrogram

in both. For phenyl methyl ether there is also a strong absorption peak at about 1270 cm^{-1}; this indicates the pressence of $-C-O-C-$ group and hence also observed in other ethers. Thus, every group has a definite absorption band in a particular range of the spectrum.

SPECTRA AND MOLECULAR CONSTITUTION

7.9. Electromagnetic Radiations

The electromagnetic radiations such as, heat, light, X-rays, radio-waves etc. have different frequencies (ν) or wavelengths (λ). These radiations are emitted or absorbed in one or more quanta of discrete amounts. The quantum of energy, $\epsilon = h\nu$, where ν = frequency of the radiation and h is Planck's constant. Hence the energy associated with different radiations would be different. In Fig. VII.9 is shown the approximate distribution of frequency, wavelength, energy, etc. amongst the various electromagnetic radiations. Thus, a quantum of X-ray radiation is more than million times larger than that of an infra-red quantum. [See also Sec. 19.3.]

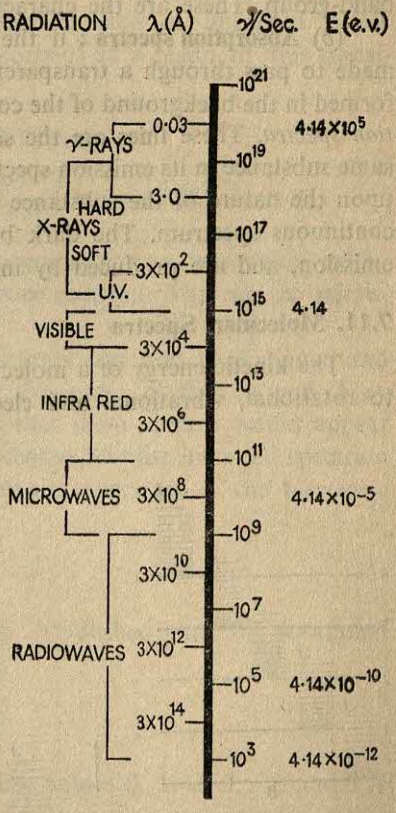


Fig. VII.9

7.10. Types of Spectra

Broadly speaking, there are two kinds of spectra : (*a*) Emission spectra and (*b*) Absorption spectra

(*a*) **Emission spectra :** When the light emitted from a source is directly led through a spectroscope, the emission spectra would be observed. There are three kinds of emission spectra, namely (*i*) continuous spectra (*ii*) line spectra and (*iii*) band spectra.

(*i*) *Continuous spectra.* The light emitted from incandescent solids gives rise to continuous spectra. Sunlight, light from carbon arc etc led through the spectroscope produce a patch of illumunation of different colours, whose bounderies are not at all sharply defined. The common example is the 'vibgyor' from sun-light. There is no gap or darkspace in such a spectrum.

(*ii*) *Line spectra.* Incandescent gases or vapours (as in a discharge tube) in the *atomic state* emit radiations which led through the spectroscope produce individual sharp bright lines in a dark background. This is the line spectra or atomic spectra. A line in the spectrum will always have the same wavelength. Each element has its own characteristic set of lines by which it can be identified. The line spectra will be discussed later.

(*iii*) *Band spectra*: Band spectra consist of broad luminous columns or bands upon a dark background. These are generally emitted by hot gases or vapours in the *molecular state*. Hence, these are called molecular spectra. One end of each band is bright and sharp and the intensity shades off towards the other end. With spectroscopes of high resolving power, each band is found to consist of innumerable closely-packed lines. Even a diatomic molecule produces an enormous number of lines. The lines in each band come closer and closer until these merge into an edge called the band-head. A number of bands clustered together form a band-group. These are the characteristics of molecular spectra.

(*b*) **Absorption spectra :** If the light from a hot source, say carbon arc, is made to pass through a transparent medium then dark lines or dark bands are formed in the background of the continuous spectrum. These are known as *absorption spectra.* These lines are the same which would have been produced by the same substance in its emission spectrum. The position of the dark lines will depend upon the nature of the substance which absorbs its characteristic lines from the continuous spectrum. The dark bands also consist of innumerable lines, as in emission, and are produced by molecules.

7.11. Molecular Spectra

The kinetic energy of a molecule (apart from its translational motion) is due to rotational, vibrational and electronic motion. The three types of energy,—rotational, vibrational and electronic—are all governed by quantum principles. Any amount of energy cannot be absorbed or emitted by a molecule. There are quantum levels for all the three kinds of energy. In increasing or decreasing the quantum level of rotation, vibration or electronic motion discrete amounts of energy in the form of one or more (whole number of) quanta of energy would be involved. The quantum levels for the three types of energy are schematically shown in Fig. VII.10. *A* and *B* are the two electronic states of a molecule. In each of the electronic states there are vibrational levels indicated by v (=0, 1, 2, 3, . . .). Again for each vibrational state there exist some rotational levels denoted by j (= 0, 1, 2, 3, . . .). A possible transition in any one of these levels will lead to a change in energy content and give rise to spectral lines.

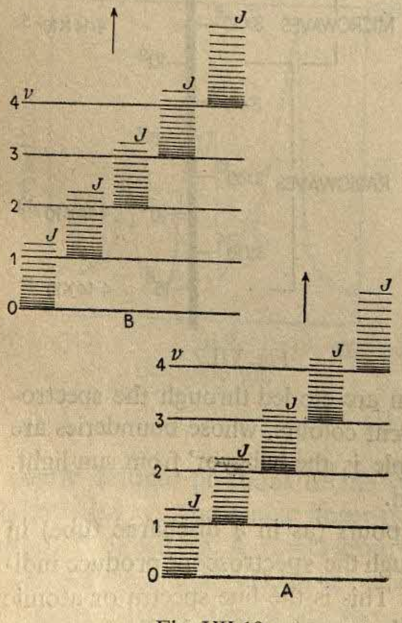


Fig. VII.10

Whenever there is a change in quantum level in any one or more of these types of energy, there would be absorption or emission of energy. There may be a change in rotational level only, or there may be a change in the vibrational level (on which rotational changes are usually superimposed); or the electronic energy level may change which is simultaneously associated with vibrational and rotational changes.

The bands in the molecular spectra are found in three distinct regions of the electromagnetic spectrum, namely (*i*) the microwave or far infra-red (*ii*) the near infra-red and (*iii*) the visible-ultraviolet regions.

(*i*) A change in the rotational quantum level involves a small energy-change of the order of 0.005 ev. The quantum of energy emitted or absorbed is $h\nu$. The wavelength of the radiation emitted (or absorbed) as a result of this transition is easily known.

$$\therefore \quad h\nu = 0.005\,\text{ev} = 0.005 \times 1.6 \times 10^{-12}\,\text{ergs}$$

$$\text{or} \quad \lambda = c/\nu = \frac{ch}{h\nu} = \frac{3\times10^{10}\times6.6\times10^{-27}}{0.005\times1.6\times10^{-12}} \approx 2.5\times10^{6}\text{Å}$$

In other words, the spectral lines would appear near the microwave region. Hence the microwave spectra is formed from pure rotation. That is, the microwave spectrum is the *rotational spectrum.*

The approximate energy required in a vibrational quantum level change and in an electronic quantum level change are of the order of 0.1 ev and 5 ev respectively. A calculation as done above show that these spectra would appear in the near infra-red and in the visible-ultraviolet region. So near infra-red spectrum is the *vibrational spectrum* and the visible-ultraviolet spectrum is the *electronic spectrum.*

7.12. Rotational Spectra

From quantum considerations, it has been established that the rotational energy at the j-th level is given by

$$E_{rot} = \frac{h^2}{8\pi^2 I} j(j+1)$$

where j is the rotational quantum number having values 0, 1, 2, 3, . . . and I is the moment of inertia of the molecule.

In the formation of absorption spectrum, the energy absorbed increases the rotational quantum level.

There are two restrictions in such rotational transitions. (*i*) The rotational transition is limited to adjacent levels, *i.e.* $\Delta j = \pm 1$. So, the rotational quantum level may increase from $(j-1)$-th level to the j-th level.

(*ii*) Pure rotational transition occurs only with polar molecules. Non-polar molecules like H_2, Cl_2, N_2, etc. have no rotational band.

For a given species of molecules; $h/8\pi^2 I$ is a constant which is denoted by B.

The rotational energy at the $(j-1)$-th level, $E_{j-1} = Bh(j-1)j$

The rotational energy at the j-th level, $E_j = Bhj(j+1)$

∴ The difference of energy between the two rotational levels,

$$\triangle E = E_j - E_{j-1} = Bhj(j+1) - Bh(j-1)j = 2Bhj$$

where j is the higher quantum level.
Now $\triangle E = h\nu$, ν being the frequency of the radiation absorbed.

Then $h\nu = 2Bhj$, or $\nu = 2Bj$

The frequencies of the different lines in the rotational spectrum are obtained by putting $j = 1, 2, 3$, etc.

$$\begin{aligned} \nu_{0\to1} &= 2B \\ \nu_{1\to2} &= 4B \\ \nu_{2\to3} &= 6B \\ \nu_{3\to4} &= 8B, \text{ etc.} \\ \therefore\ \triangle\nu &= 2B \end{aligned}$$

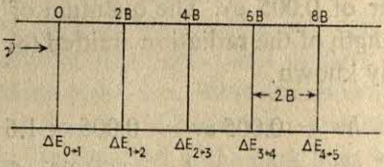


Fig. VII. 11

The spectral lines are equispaced. Measurement of frequencies give the value of B. Since $B = h/8\pi^2 I$, the moment of inertia $I\ (= Mr^2)$, and the bond distance r for a diatomic molecule (say) are easily found out.

7.13. Vibration-rotation Spectra

The vibrational energy in the v-th quantum level is given by

$$E_{vib} = (v + \tfrac{1}{2})\,h\omega$$

where ω is the fundamental frequency of vibration. In a vibration-transition from quantum level v' to v, the energy-change

$$\triangle E_{vib} = (v' - v)h\omega$$

Pure vibrational transition without affecting rotation is not permitted. A vibrational transition is associated with rotational changes. In other words, a rotational energy change is superimposed on the vibrational energy-change. Hence

$$\triangle E = \triangle E_{vib} + \triangle E_{rot}$$

or $$h\nu = (v' - v)\,h\omega \pm 2Bhj$$

or $$\nu = (v' - v)\,\omega \pm 2Bj$$

Due to anharmonicity, change in vibrational levels may be, $\triangle v = v' - v = 1, 2, 3, \ldots$. The rotational level change is always $\triangle j = \pm 1$.

Putting different values of v' and j, innumerable values of ν, the frequency of the absorbed (or emitted) radiation, are obtained. That is why a large number of lines are found in the infra-red vibration spectra.

From the infra-red spectra, many a valuable information are obtained, such as, the moment of inertia, bond-distance, heat of dissociation etc.

The regular recurrence of some absorption bands when certain groups are present in the molecule points to the fact that these bands are characteristic of those groups. The experimental determination of the absorption peaks thus enables one to confirm the presence of definite functional groups in the molecule under investigation. The characteristic frequencies of some of the groups are tabulated below:

TABLE

Group	$\bar{\nu}\ cm^{-1}$
$\overset{\diagdown}{-\mathrm{C}-\mathrm{H}}$	2880–3030
$\overset{\diagup}{=\mathrm{C}-\mathrm{H}}$	3000—3120
$\overset{\vert}{\equiv\mathrm{C}-\mathrm{H}}$	3340
$\underset{\diagup}{\overset{\diagdown}{\mathrm{C}=\mathrm{O}}}$	1660–1870
$\underset{\diagup}{\overset{\diagdown}{\mathrm{C}=\mathrm{C}}}$	1600–1680
$-\mathrm{C}\equiv\mathrm{C}-$	2200–2260
$-\mathrm{O}-\mathrm{H}$	3500–3700
$\underset{\diagup}{\overset{\diagdown}{\mathrm{N}-\mathrm{H}}}$	3300–3500

These are most useful in confirming the presence of a group in a molecule. In a mixture, the positions and intensities of the bands for a particular substance are not affected by the presence of other components. So, in a mixture of closely related compounds, the identification as well as the quantitative estimation of a particular component can be spectroscopically ascertained, even if the chemical methods fail.

7.14. Electronic Spectra

The absorption of radiation by a molecule in the visible-ultraviolet region which involves high energy values gives rise to the electronic spectra. The electrons from a lower energy level get excited to the higher one. The electronic spectra even of a diatomic molecule is very complex. Any change in the electronic state is associated with simultaneous vibrational and rotational levels.

When an electronic state is altered, there is usually a large number of changes in vibrational levels, each of which gives rise to a band. In each of these bands again there are innumerable lines due to rotational transitions. This makes the electronic spectra, even of very simple molecules, quite complicated.

Now, the energy of the molecule

$$E = E_{el} + E_{vib} + E_{rot}$$

In two electronic states, we can express them, as

$$E = E_{el} + (v + \tfrac{1}{2})h\omega + Bhj(j + 1)$$

and

$$E' = E'_{el} + (v' + \tfrac{1}{2})h\omega' + B'hj'(j' + 1)$$

where v and v' are the vibrational quantum levels in two states with different fundamental frequencies ω and ω'; the rotational constants B and B' consequently will be different. Subtracting,

$$h\nu = \triangle E = h\nu_e + (v + \tfrac{1}{2})h\omega - (v' + \tfrac{1}{2})h\omega' + Bhj(j + 1) - B'hj'(j' + 1)$$

where $E_{el} - E'_{el} = h\nu_e$, *i.e.*, the energy of the radiation absorbed or emitted had there been pure electronic energy-change.

On the other hand, the change in vibrational level ($\triangle v = v - v'$) may have any integral value,

$$\triangle v = 0, \pm 1, \pm 2, \pm 3, \pm 4 \ldots \text{etc.},$$

whereas, the rotational transitions for any of these vibrational bands, $\triangle j = \pm 1$.

Putting different numerical values of v, v', j and j', enormous number of ν-values would be available. That is why electronic spectra are so complex.

XII.9. Raman Spectra

When a beam of monochromatic light is passed through a transparent medium, a portion of light is scattered in all directions. The frequency of the scattered rays is the same as that of the incident beam. This is known as Rayleigh scattering. But a careful spectroscopic examination of the scattered rays reveals some faint lines other than those due to Rayleigh scattering. That is, a small portion of the rays are scattered with a different frequency. This was first observed by Raman in 1928 and the phenomenon is called *Raman scattering*.

An explanation of the Raman effect, based on quantum theory, may be made as follows: A molecule initially at level A with energy E_A absorbs the quantum of radiation $h\nu_i$ and is raised to the level X temporarily; ν_i is the frequency of the incident radiation. Then the energy at level X is $E_A + h\nu_i$. The molecule then emits a radiation of a different frequency (ν_s) and comes down to the level B. The energy of the molecule (E_B) now is $E_A + h\nu_i - h\nu_s$.

i.e., $$E_A + h\nu_i - h\nu_s = E_B$$

or $$h\nu_i - h\nu_s = E_B - E_A$$

or $$h\triangle\nu = E_B - E_A$$

That is, the energy which has been transferred to the molecule is $h\triangle\nu$. The change in frequency corresponding to this energy change is $\triangle\nu\ (= \nu_i - \nu_s)$. This frequency-change is called the *Raman frequency*.

Generally ν_s is less than ν_i, *i.e.*, energy is taken up by the molecule $(E_B > E_A)$. But it is also found that sometimes the molecule emits more energy than it absorbs. The result is that $h\nu_s > h\nu_i$.

The Raman-scattered lines with lesser energy, *i.e.*, those which are formed on the long wavelength side are called *stokes lines* and those which are formed on the short wavelength side of the incident beam are called *antistokes lines*.

There are however some interesting characteristics in Raman scattering. The Raman frequency is independent of the frequency of the incident radiation and depends only on the medium. For this reason, any convenient source of radiation can be used. Although the frequency-shifts correspond to the infra-red region, these are very easily investigated and determined from the scattering in visible regions. Homopolar molecules cannot exhibit vibration-spectra but these respond to Raman scattering. In rotational Raman scattering, the quantum levels change by two instead of one, *i.e.*, $\triangle j = \pm 2$.

A wealth of information is available from the study of Raman spectra. The most important application of Raman effect is in the determination of the constitution of organic molecules. As in infra-red spectroscopy, definite Raman frequencies are associated with different linkages and these are the same as in vibrational spectra. The Raman frequencies for C—H linkage is about 2800 cm^{-1} and those for $C \equiv C$ about 2100 cm^{-1}, for $C = C$ about 1600 cm^{-1} and so on. The results of examination of Raman scattering are thus helpful in establishing the constitution of an organic molecule.

Halides like NaCl, KCl, $CaCl_2$, etc. do not show any Raman frequency, but non-metallic chlorides and chlorides like $HgCl_2$, Hg_2Cl_2, $ZnCl_2$, etc. have intense Raman lines. This proves the existence of vibrational levels in Hg_2Cl_2, etc. confirming their covalent nature.

EXERCISES

1. What are *additive* and *constitutive* properties? Explain them with examples.

2. Explain molar refraction and atomic refraction. In what units are these expressed?

3. What is molar polarisation? Is it different for polar and non-polar molecules? Is molar polarisation dependent on temperature?

4. Define and explain the terms (*i*) dipole moment (*ii*) bond moment. Illustrate with an example the relation between the two.

5. Give an outline of a method for the determination of dipole moment.

6. Write notes on : (*i*) orientation polarisation, (*ii*) bond moments, (*iii*) optical density and (*iv*) molar extinction coefficient.

7. State Beer's Law and explain its significance. How will the optical density change if the concentration of the solution is halved and its thickness doubled.

8. Illustrate the scope of *IR* and *UV* spectroscopy in elucidating the structure of a molecule.

9. Critically examine and give your views about the following statements:

(*a*) *ABA* type triatomic molecules are always non-polar

(*b*) Orientation polarisation is directly proportional to temperature

(c) The extinction coefficient depends upon the concentration but is independent of the wave-length of the radiation used.

10. What is an absorption spectrum? What informations are available from such spectra? Discuss the relation of absorption spectrum with chemical constitution.

11. Discuss the principles underlying infra-red spectroscopy.

12. Show how you would proceed to find out the moment of inertia of a diotomic molecule.

13. Explain the origin of a Raman spectrum and illustrate its application in the elucidation of molecular structure.

14. How is the information from rotational spectral lines used in calculating the bond length of a diatomic molecule?

CHAPTER 8

THERMODYNAMIC PRINCIPLES

THE FIRST LAW OF THERMODYNAMICS

8.1. Introduction

Thermodynamics, literally speaking, means flow of heat and its transformations. Heat is a form of energy. At present, thermodynamics is not concerned with heat energy alone, but it includes the study of all types of energy-changes and their transformations associated with physical or chemical processes.

Thermodynamics is based on three simple laws. These laws are not derived from any assumption. These laws are generalisations from long experience with energy. Yet these laws could be subjected to rigorous mathematical operations. They yielded formulations which were confirmed by experiments. These have been tested in various fields, from steam-engines to ezymatic reactions, and have been found to be rigidly valid.

The approach in thermodynamics is entirely different from that in the kinetic theory. It only recognises the observable properties of matter, such as pressure, temperature, etc without assumptions of its molecular existence. The properties of the bulk-matter are employed to explain the different chemical or physical processes. Thermodynamics does not concern itself with time variable, and as such it has little application in the study of rate processes such as, diffusion, viscous flow, etc.

The chemical processes are always accompanied with energy-changes and thermodynamics plays a fundamental role in the understanding of these processes. Thermodynamics not only gives the quantitative relations in the inter-conversion of different forms of energy but it also predicts whether a change would occur, and if so, to what extent. It explains the conditions under which a system would remain in equilibrium. It can forecast if any work or benifit would be available from a transformation under a given set of conditions.

Before starting with the laws of thermodynamics, it is necessary to define some of the most commonly used terms in its discussions.

8.2. Thermodynamic Systems

In thermodynamics, a *System* is defined as an object or a quantity of matter, *i.e.*, a part of universe, chosen, for observation, separately from the rest of the universe. The system is enclosed by a boundary which separates it from the rest of the universe. All other parts of the universe, outside the boundary of the system, are called the *surroundings*.

A system is said to be an *isolated system*, when it is incapable of exchanging either energy or matter with the surroundings.

A *closed system* is one in which energy-exchange with the surroundings is possible but no mass transfer across the boundary is permitted.

In an *open system*, the transfer of both mass and energy across the boundary is possible.

Properties of a system : The physical characteristics which are experimentally measurable and which enable us to define a system are called *thermodynamic parameters* or *properties* of the system. Various properties, such as pressure, volume, temperature, composition, refractive index, viscosity, dielectric constant, surface tension, etc. are associated with a system. But ordinarily for thermodynamic consideration, only the first four parameters namely, *pressure, volume, temperature and composition* are of fundamental importance and are used.

In a given system of definite composition, the system would be defined by three variables, P, V and T. But these three variables are inter-related by some equation of state. For example, for an ideal gas, the relation is $PV = RT$. Hence a property (X) of the given system (say energy) can be expressed by any two of the three variables, *i.e.*,

$$X = f(P, T), \quad \text{or} \quad X = f_1\,(V, T) \quad \text{or} \quad X = f_2\,(P, V)$$

The properties of the system which are dependent upon the mass of the system such as volume, energy, surface area, etc. are called *extensive properties.* On the other hand, properties like pressure, density, temperature, etc. are independent of the mass of the system and are called *intensive properties.*

Of these properties, temperature plays a predominant role in thermodynamic functions. It will be seen that temperature controls transfer of heat as well as influences the transformation of energy to a large extent. Though obvious, one fact may be mentioned here. If A, B, C are three systems such that A is in thermal equilibrium with B and C is also in thermal equilibrium with B, then A and C would also be in thermal equilibrium. The temperatures of the three systems would be the same. This is stated as *Two systems in thermal equilibrium with a third are in thermal equilibrium with each other*. This is known as the *Zeroth law of thermodynamics.* All our temperature measurements and description are based on the truth of this principle.

The state of system is expressed by assigning definite values to the thermodynamic properties of the system. When a system undergoes a change, one or more of its thermodynamic variables would also change. If as a result of series of changes, the system returns to its initial state, its thermodynamic parameters would also return to their original values. Such a process is called a *cyclic process.*

If a change takes place in such a way that the temperature remains constant throughout, it is called an *isothermal process.* On the other hand, the change occurring in a thermally insulated system which do not permit heat exchange with the surroundings, is called an *adiabatic process.*

Equilibrium State: A system is said to be in a state of equilibrium when (*i*) its composition remains fixed and definite (*ii*) the temperature at all parts of the system is the same and also identical with that of the surroundings and (*iii*) there is no unbalanced force between different parts of the system or between the system and the surroundings. Therefore, a system at equilibrium must have a definite pressure, temperature and composition.

8.3. Work, Energy and Heat

The idea of *Work* comes to us intuitively, say, from the performance of a machine or from the application of mascular effort to move a body. Mathematically expressed, work (w) is the product of applied force (F) and the displacement ($\triangle l$) in the direction of the force, *i.e.*,

$$W = F \times \triangle l, \text{ (dynes} \times \text{cm} = \text{ergs)}$$

The work may be produced in diverse ways. When a gas expands by a volume ($\triangle V$) against a constant pressure (P) the work

$$W = P \times \triangle V$$

Similarly, winding of a spring, turning of a wheel, the lifting of a weight, etc., all involve work. If a quantity of electricity (Q) be transported along a wire under an electromotive force (E), the work $= E \times Q$ (volt-coulombs). Work is always the product of two factors: (*i*) the *intensity factor*, which is a measure of the force or the resistance to be overcome such as pressure P, electromotive force E, etc. (*ii*) the *capacity factor*, the extent of change or transport occurred, such a volume-change ($\triangle V$), charge transported (Q), etc.

When we push a body through some distance by our hand the work is obtained from our mascular energy. When the fan overhead rotates the mechanical energy of its motion or work is derived from electrical energy. These illustrate work is obtainable from different forms of energy. Again two stones are rubbed against one another, the mechanical energy (or work) is at least partly transformed into heat. The work done in the turning of the blades of a turbine produces electricity. These illustrate that work can be converted into different types of energy.

Hence, *Energy is defined as a property which can be transformed into or produced from work.*

Energy manifests itself in various forms, such as thermal, electrical, chemical, radiant, mechanical (potential and kinetic), internal, surface energy, etc. From the definitions of energy, work itself is an observable form of energy. In fact, often the different forms of energy are expressed in terms of work.

Heat is also a very easily available form of energy but it is somewhat different from other forms of energy, such as, electrical, chemical, etc. Other forms of energy can be completely converted into work under suitable conditions. But *heat* cannot be wholly transformed into work, only a portion of it can be rendered into work.

8.4. Internal Energy

A material system must possess a store of energy. This is evident from observations in diverse systems, e.g., (*a*) a gas condenses into its liquid state yielding heat energy (*b*) zinc and copper sulphate react in a Daniell cell producing electrical energy. (*c*) steam expands from a higher to a lower pressure in an engine yielding work or mechanical energy, etc. Unless the systems had inherent energy within how could they yield work or other forms of energy by themselves. Hence, every system has within itself a quantity of energy. This energy is called *internal energy* of the system and is denoted by the symbol, E. The magnitude of the internal energy (E) of a given system depends upon the three variables (P, V, T) of the system. Hence, we have

$$E = f(P, T) \quad \text{or} \quad E = f_1(P, V) \quad \text{or} \quad E = f_2(V, T)$$

Character of the Internal Energy : (*i*) the internal energy is a property of the system entirely defined by the parameters. Whenever the system is in the same thermodynamic state, its internal energy will have the same value. E is thus a single-valued function of the thermodynamic state of the system and is independent of its previous history.

(*ii*) The internal energy is an extensive property increasing directly proportionally with increase in mass.

(*iii*) When a system changes from a thermodynamic state $A(P_1, V_1, T_1)$ to a thermodynamic state $B\,(P_2, V_2, T_2)$, its internal energy will change from E_A to E_B. The value of E_A depends on P_1, V_1, T_1 and that of E_B on P_2, V_2, T_2. Hence the change in internal energy, $\triangle E\ (= E_B - E_A)$ will be governed by the magnitudes of the variables in the final and in the initial states only. $\triangle E$, will be always independent of the way or path along which the change is effected. A particular change may be made in different ways, but $\triangle E$ will always be the same (Fig. VIII.1).

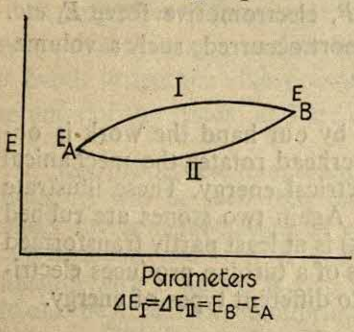


Fig. VIII.1

(*iv*) When a system suffers a series of changes and finally returns to the initial state, it is called a *cyclic process*. The internal energy will have the same magnitude as its initial value, irrespective of what happened meanwhile. If all the $\triangle E$-values of the different steps of the cyclic process be summed up, then $\Sigma \triangle E = 0$. Hence, $\oint dE = 0$; the circle on the integral denotes cyclic process.

8.5. State Functions

A function, like internal energy E, whose magnitude is governed only by the state of the system (P, V, T) and nothing else, is called a *state function*. The change in the value of the state function for a specified transformation of the system is independent of the way by which the transformation occurs, Thus, internal energy E is a state function. Later on, we shall come accross other functions associated with a system, such as entropy, enthalpy, free energy, etc. which are also 'state functions'.

In contrast, there are thermodynamic quantities whose values depend on the way the transformation is carried out. Suppose the temperature of a mass of water is to be raised from $T_1°$ to $T_2°$. This can be accomplished in different ways, (Fig. VIII.2)

(*i*) Directly q calories of heat may be introduced (A)
(*ii*) A quantity of electricity may be passed through a coil immersed in the given system of water (B)
or (*iii*) A paddle-wheel may be mechanically rotated in the water, as in the historical experiment of Joule, by repeated lowering of a weight (C).

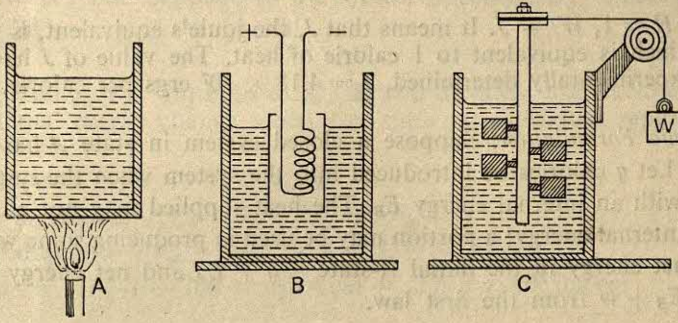


Fig. VIII.2

Though the change of the system in each case is the same, (*i*) the heat input (q) is nil in the process (B) or (C), whereas (*ii*) work input (w) in either process (A) or (B) is nil. Though it has a definite value in path (C). It is thus seen that heat-change q, or work involved w in a process depend on the path of transformation of the system. Hence, these are called *path functions*; these are not state functions.

8.6. First Law of Thermodynamics

It is common knowledge that different forms of energy are all interconvertible; heat is transformed into work (steam engines), chemical energy is changed into electricity (battery), electricity is transformed into work and light (electric fans and bulbs) and so on.

Very careful quantitative measurements of energy-changes in such transformations were carried out by Mayer, Joule, Kelvin and many others. It was always found that when one kind of energy disappears an exactly equivalent quantity of another kind appears neither more nor less. That is, energy cannot be annihilated nor can it be created out of nothing. Hence, transformation of energy occurs but the quantity remains constant.

Further all attempts to construct a *perpetual motion machine of the 1st kind,* which would yield work continuously without expenditure of any energy or fuel, failed. The experience is that out of nothing energy or work cannot be obtained.

Since disappearance of an energy brings out an equivalent amount of another kind, the net energy of the system would remain constant. This is formally stated as:

The total energy of an isolated system remains constant and whenever a quantity of one kind of energy disappears, an exactly equivalent quantity of some other kind must make its appearance.

This is the *first law of thermodynamics.* Since the total energy remains unaltered, this is also called the *law of conservation of energy.* This law is thus the result of experience and has never been found to fail; it is indeed a law of nature.

The principle further suggests that if heat (H) is obtained from work (W) or *vice versa*, then the amount of heat produced would be proportional to the work spent. That is,

$$W = JH, \text{ where } J \text{ is the constant of proportionality}$$

When $H = 1$, $W = J$. It means that J, the joule's equivalent, is the amount of work which is equivalent to 1 calorie of heat. The value of J has been very carefully experimentally determined. $J = 4.18 \times 10^7$ ergs per calorie.

Algebraic Formulation: Suppose a closed system in state A has an internal energy E_A. Let q calories be introduced into the system when the system changes to state B with an internal energy E_B. The heat supplied may not all be used in increasing internal energy; a portion may be used in producing some work (w).

Now net energy in the initial A-state $= q + E_A$ and net energy in the final B-state $= E_B + w$ from the first law.

$$q + E_A = E_B + w$$

or
$$q = E_B - E_A + w = \triangle E + w \qquad \ldots \text{(VIII.1)}$$

i.e. heat absorbed = internal energy increase + work done by the system for infinitesimal changes, we may write

$$dq = dE + w \qquad \ldots \text{(VII.2)}$$

In evaluating such changes,

(*a*) heat absorbed by a system is regarded as positive and heat expelled from the system is negative.

(*b*) The increase in internal energy of the system is positive and the decrease is negative.

(*c*) Work done by the system, *i.e.* work obtained from the system during a change is positive. But the work done on the system by the surrounding during a change is regarded as negative.

Suppose the system undergoes a small volume-increase dV under a constant pressure P, then work obtained would be PdV. Hence from the first law:

$$dq = dE + PdV \qquad \ldots \text{(VIII.3)}$$

The equations given above are the mathematical expressions of the first law. A few comments may be made on these equations.

(*a*) In an *adiabatic process*, no heat can be supplied to the system, *i.e.*, $q = 0$, hence

$$\triangle E + w = 0; \qquad \text{or} \qquad w = \triangle E \qquad \ldots \text{(VIII.4)}$$

It means that the work obtained from the system is equal to the decrease in internal energy.

(*b*) In a *cyclic process*, the system returns to its initial state and so the internal energy also has the initial value, *i.e.* $\triangle E = 0$. Hence, $q = \triangle E + w = w$
That is, the work obtained from the system is exactly equal to the heat supplied for the whole cycle.

(*c*) In a process at *constant volume*, $\triangle V = 0$, if the work involved is all mechanical, *i.e.*, only expansion or contraction of the system, then work $P\triangle V = 0$,

$$\therefore q_v = \triangle E + P\triangle V = \triangle E \qquad \ldots \text{(VIII. 5)}$$

It means that the heat supplied to the system is completely utilised in the increase of internal energy of the system.

Problem: A liquid ($M = 78$) boils at 353°K and its lalent heat is 95 cal/gm. calculate the internal energy change when one mole of the liquid vaporises at its b. pt.

the heat absorbed, $q = 78 \times 95 = 7410$ cal

The change in volume $\triangle V = V_g - V_{liq} = V_g$

$\therefore$ work produced $= PV_g = RT = 2 \times 353 = 706$ cal

$\therefore \triangle E = q - w = 7410 - 706 = 6704$ cal $= 2.816 \times 10^4$ joules

8.7. Reversible and Irreversible Processes

The change of a system from one state to another may occur either in a reversible or in an irreversible way. In *a reversible process*, the change of the system is allowed to happen slowly in minute quantities until the whole of the specified change is achieved. In an ideally reversible process, the change must occur in successive stages of infinitesimal quantities. The small changes should be carried out in such a way that, throughout the transition, the system must be maintaining virtual thermodynamic equilibrium, at each of the small stages. Moreover, a reversible process must be such that if the system change in the opposite direction back to the initial condition along the same path and the magnitudes of the changes of the thermodynamic quantities in the different stages will be the same as in the forward direction but opposite in sign.

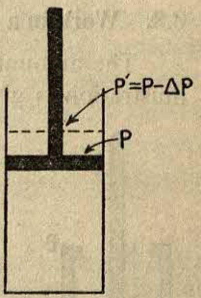


Fig. VIII.3

Suppose a gas is enclosed in a cylinder with a piston and kept in a constant temperature bath. The pressure over the piston is P. The gas will expand if the pressure P is very slightly lowered to P'. Let the work of expansion be w. If now the new pressure be raised slightly, back to P, the gas will contract. It can be shown that the work now performed on the gas during contraction will be the same as received from the system during expansion. Such a change would be regarded as a reversible one.

An irreversible process is one which occurs suddenly or spontaneously without the restriction of occurring in successive stages of infinitesimal quantities. The system would also not remain in virtual equilibrium during the transition. The system after undergoing a change will not have the tendency to return to the initial state by iteself. If the change be reversed and the system is made to go back to the initial state, the work (w) in the forward direction and in the backward process would be unequal. It is important to remember that if the initial and final stages be specified, the internal energy change would always be the same, whether the process has been effected reversibly or irreversibly. In an irreversible process, since work terms (*dw*) in the two opposite directions are unequal, the heat-transfers (*dq*) would also be unequal.

Many processes occur in nature spontaneously. These spontaneous processes happen unidirectionally and certainly not in successive stages of equilibria in minute quantities of transformation. Natural processes are therefore all irreversible.

Suppose water in a beaker is heated from 20°C by heating over a Bunsen flame. This process is irreversible, because the temperature of the flame is very high and the water near the bottom of the beaker will be more quickly heated than the rest.' In consequence, convection and turbulence would start. As such, the equilibrium is disturbed and the change is not reversible.

The water from the slopes of the Himalayas flows down the Ganges into the Indian Ocean. Such natural flow of a liquid downwards is spontaneous and is irreversible. The water in the Indian Ocean will of itself never go up the hill. If the water is pushed up from the Ganges by external agencies, the work to be done far exceeds the work received duting its downward flight. Hence the process is irreversible.

A gas like ammonia brought in contact with water will spontaneously be absorbed by water forming a solution, producing heat and particularly no work. Of itself, the solution would not separate back into the two components water and the gas. A lot of work has to be performed to separate these two from the solution.

A reversible process is that in which the opposite change can be effected along the same path with heat-changes and work performed being the same though opposite in sign, and as such the process has to be carried out in successive stages of equilibrium in small amounts. An irreversible process would not satisfy these conditions.

8.8. Work in a Reversible Process

The amount of work involved in a reversible process can be evaluated. An illustration is given here.

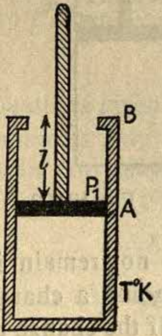


Fig. VIII.4

Expansion of a gas. Suppose *n* moles of a perfect gas is enclosed in a cylinder by a frictionless piston (Fig. VIII.4). The whole cylinder is kept in a large constant-temperature bath at T°K. Any change that would occur to the system would be isothermal. There is a latch at the top *B*, and the piston cannot move beyond that. The volume of the gas when the piston is at *B* is V_2 (suppose). To begin with, the gas has a volume V_1 and the piston is at the point *A*. The aim is to expand the gas from volume V_1 to volume V_2. The work of expansion (*w*) will be given by the product of opposing force and the displacement.

This expansion can be achieved in various ways. We can make the pressure over the piston arbitrarily anything, say, zero (0), $\frac{1}{2}p_1$, $\frac{1}{3}p_1$, and so on. When the pressure is zero, the work will be nil. If pressure is $\frac{1}{2}p_1$, the work will be $\frac{1}{2}p_1(V_2-V_1)$; if the pressure be $\frac{1}{3}p_1$, work would be $\frac{1}{3}p_1(V_2-V_1)$; and so on. We would receive different amounts of work from the same change. Evidently, these processes would be irreversible.

But we can carry out the process in the following way. Let the pressure p_1 be reduced by an infinitesimal amount dp. Let the new pressure be $p_1' = p_1 - dp$. The work would be $dw = (p_1 - dp)\, dv$. The change in volume would be small and equal to dv. The new pressure be again reduced slightly so that it changes to $p'' = p'_1 - dp$, then the work would be $dw = (p_1' - dp)dv$.

This process may be repeated and by such infinite number of successive steps, the gas may be made to expand from volume V_1 to V_2. The net work for all the minute stages is given by

$$\int dw = \Sigma(p-dp)dv = \int_{V_1}^{V_2} pdv - \int_{V_1}^{V_2} dpdv = \int_{V_1}^{V_2} pdv$$

since dp and dv are infinitesimal quantities, $dp.dv$ is negligible.

$$\text{or} \qquad w = \int_{V_1}^{V_2} pdv = \int_{V_1}^{V_2} \frac{nRT}{v}\, dv$$

$$\text{or} \qquad w = nRT\, ln\, \frac{V_2}{V_1} = nRT\, ln\, \frac{P_1}{P_2} \qquad \ldots \text{(VIII.6)}$$

since $V_2/V_1 = P_1/P_2$ in an isothermal expansion of a perfect gas.

For 1 mole of an ideal gas; $w = RT\, ln\, (V_2/V_1)$

This work is necessarily the product of the force and the displacement. The displacement in this case is specified, namely $(V_2 - V_1)$. Hence, the greater the magnitude of the force or pressure, the greater would be the magnitude of work. If the pressure over the piston were made greater than $(P_1 - dP)$, there obviously would be no expansion. Therefore if we want to have the desired expansion $(P_1 - dP)$ is the maximum that could be applied. So, the work obtained in equation (VIII.6) is the maximum. If the pressure over the piston were made appreciably less, instead of infinitesimally smaller than the gas pressure, the work would be evidently less than that obtained above and the process also would be more irreversible. We are therefore led to conclude that the work in the reversible process is the *maximum* and is greater than that in the irreversible process.

Reversible work is greater than the irreversible work: Suppose we carry out a small expansion of the same gas in two ways. Firstly, we change the volume as before until the pressure is P_2, the process is reversible and the reversible work is given by,

$$W_r = RT\, ln\, \frac{V_2}{V_1} = RT\, ln\, \frac{P_1}{P_2}\,; \qquad \text{(for 1 mole)}$$

Secondly, we reduce the pressure over the piston at once to P_2 which would be the equilibrium pressure of the gas when the volume is V_2, then the gas would immediately expand against a constant pressure P_2, the process is irreversible and the irreversible work

$$W_{ir} = P_2(V_2 - V_1) = P_2\left[\frac{RT}{P_2} - \frac{RT}{P_1}\right] = RT\left[1 - \frac{P_2}{P_1}\right]$$

Then, $$W_r - W_{ir} = RT\,ln\,\frac{P_1}{P_2} - RT\left[1 - \frac{P_2}{P_1}\right]$$

$$= RT\frac{P_1-P_2}{P_2} - RT\frac{P_1-P_2}{P_1} \text{ (for small changes)}$$

$$= RT(P_1-P_2)\left[\frac{1}{P_2} - \frac{1}{P_1}\right] = \frac{RT}{P_1P_2}(P_1-P_2)^2 = + \textit{ve} \text{ quantity}$$

Hence $W_r > W_{ir}$

The work in a reversible process is greater than that in an irreversible process.

The system we were considering expanded to a volume V_2 and pressure P_2. Let the system now return to its original state reversibly. The pressure has to be increased successively in infinitesimal amounts until the volume is V_1 and pressure P_1. The work to be done would be, as before,

$$\int dw = \Sigma(p + dp)dv = \int_{V_2}^{V_1} pdv \quad \text{(since } dp.dv \text{ is negligible)}$$

$$\therefore \quad w = nRT\,ln\,\frac{V_1}{V_2}$$

This is equal and opposite to the work obtained during expansion. Hence net work in the reversible cyclic process is Zero.

It is seen that

(*i*) *A change carried out in a reversible way yields maximum work. Conversely in order to obtain maximum work the change must be effected in a reversible fashion.*

(*ii*) *The net work in an isothermal reversible cyclic process is zero.*

8.9. Enthalpy or Heat Content

The product of pressure (P) and volume (V) of a system is expressed as energy. The sum of the two energy quantities associated with the system, namely the internal energy (E) and the PV-energy, is universally represented by the symbol H and is called the *enthalpy or heat-content* of the system.

$$H = E + PV \qquad \ldots \text{(VIII.7)}$$

E, the internal energy, depends only on the parameters of the system and P, V are themselves parameters. Hence, H would depend on the parameters only and is therefore a *state function*. When a system changes its state, the enthalpy H also changes. And because H is a state function, hence enthalpy-change $\triangle H$ will be independent of the path or the way of change.

In the differential form, $dH = dE + PdV + VdP$ ... (VIII.8)

If the system undergoes a change at *constant pressure*, then

$$dH_p = dE + PdV_p \qquad \ldots \text{(VIII.9)}$$

The suffix p is used to indicate constancy of pressure.

If during the change the work is all mechanical (expansion or contraction), then at constant pressure,

$$w_p = PdV_p$$

Substituting, $dH_p = dE + PdV_p$

$= dE + w_p = dq_p$ (from the 1st law)

$\therefore$ For a finite process,

$$q_p = \triangle H_p \qquad \ldots \text{(VIII.10)}$$

The function enthalpy (H) is such that its change is equal to the heat absorbed at constant pressure by the systems during the change.

Problem: At 27°C, 3 moles of an ideal gas was allowed to expand isothermally and reversibly from 1 litre to 10 litres. calculate the work obtained.

$$w = nRT\, ln \frac{V_2}{V_1} = 3 \times 0.0821 \times 300 \times 2.303 \log \frac{10}{1}$$
$$= 170.17 \text{ litre-atm.}$$

Problem: The latent heat of vaporisation of Bromine at 59°C and 1 atm is 29.2 kj/mole. Find $\triangle H$ and $\triangle E$ for the process of vaporisation of one mole.

Latent heat, $L = \triangle H = q_p = 29.2\, kj$

Work in vaporisation, $w = P\triangle V = P(V_g - V_l) = PV_g$

$= RT = 8.32 \times 10^{-3} (kj) \times 332$

$= 2.76\, (kj)$.

$\therefore \quad \triangle E = \triangle H - P\triangle V = \triangle H - w = 29.2 - 2.76 = 26.44\, kj$

8.10. Heat Capacity

The amount of heat required to raise the temperature of one gm of a substance by 1°K is called its *specific heat*. The heat input required to raise the temperature of one mole of the substance by 1°K is called its molar heat-capacity or simply *Heat Capacity*. The heat capacity is denoted by C.

If dq heat is required for dT increase in temperature for one mole of the substance, then

$$C = \frac{dq}{dT}$$

But dq is a path function and its value depends on the actual process followed. We can place certain restriction to obtain precise values of heat capacity. The usual restrictions are 'at constant pressure' and 'at constant volume'. So that, we have

$$C_v = \frac{dq_v}{dT} \quad \text{and} \quad C_p = \frac{dq_p}{dT}$$

But $dE = dq_v$ and $dH = dq_p$ (Eqns. VIII 5 and 10)

Hence $C_v = \left(\frac{\partial E}{\partial T}\right)_v$ and $C_p = \left(\frac{\partial H}{\partial T}\right)_P$ ... (VIII.11)

For finite processes,

$$\left.\begin{aligned} &\text{at constant volume,} \quad \triangle E = C_v \triangle T \\ &\text{at constant pressure,} \quad \triangle H = C_p \triangle T \end{aligned}\right\} \qquad \ldots \text{(VIII.12)}$$

assuming C_v, C_p remain unaltered in the temperature range involved.

8.11. Relation between C_P and C_V.

The relation between the two heat capacities may be easily derived. By definition,

$$E = f(V, T)$$

$$\triangle E = \left(\frac{\partial E}{\partial T}\right)_v \triangle T + \left(\frac{\partial E}{\partial V}\right)_T \triangle V$$

Hence $$\left(\frac{\partial E}{\partial T}\right)_P = \left(\frac{\partial E}{\partial T}\right)_v + \left(\frac{\partial E}{\partial V}\right)_T \left(\frac{\partial V}{\partial T}\right)_P$$

Then $$C_P - C_V = \left(\frac{\partial H}{\partial T}\right)_P - \left(\frac{\partial E}{\partial T}\right)_V$$

$$= \left(\frac{\partial E}{\partial T}\right)_P + P\left(\frac{\partial V}{\partial T}\right)_P - \left(\frac{\partial E}{\partial T}\right)_V$$

$$= \left(\frac{\partial E}{\partial T}\right)_V + \left(\frac{\partial E}{\partial V}\right)_T \left(\frac{\partial V}{\partial T}\right)_P + P\left(\frac{\partial V}{\partial T}\right)_P - \left(\frac{\partial E}{\partial T}\right)_V$$

$$= \left[\left(\frac{\partial E}{\partial V}\right)_T + P\right]\left(\frac{\partial V}{\partial T}\right)_P \qquad \text{. . . (VIII.13)}$$

The relation (eqn. VIII.13) is true for all systems. If the system be one of an *ideal gas*, where $\left(\frac{\partial E}{\partial V}\right)_T = 0$, (see next section,)

then $C_P - C_V = \left[\left(\frac{\partial E}{\partial V}\right)_T + P\right]\left(\frac{\partial V}{\partial T}\right)_P = P\left(\frac{\partial V}{\partial T}\right)_P$.

Since $PV = RT$, hence $\left(\frac{\partial V}{\partial T}\right)_P = \frac{R}{P}$

∴ For an ideal gas, $C_P - C_V = P\left(\frac{\partial V}{\partial T}\right)_P = P \times \frac{R}{P} = R$

The same result was previously found from kinetic theory considerations.

8.12. Joule's Experiment : Ideal Gases

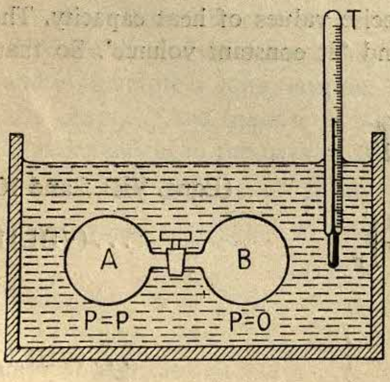


Fig. VIII.5 Joule's experiment.

Gay Lussac and, later on, Joule carried out some interesting but simple experiments to find out the internal energy-change of a gas. Two bulbs A and B connected by a stop-cock at the middle (Fig. VIII.5) were kept immersed in the water of a bath. Initially the bulb A was filled with a gas and B was practically evacuated. When thermal equilibrium was established, the stop-cock was opened. The gas readily passed into B. Since the gas expanded against zero pressure, work,

$$w = 0$$

Very careful and repeated observations revealed no change in the temperature of the bath or the bulbs; *i.e.*, $dq = 0$.

Hence, from the 1st law;

$$dE = dq - w = 0$$

Now $\qquad E = f(V,T)$

Hence, $\qquad \Delta E = \left(\frac{\partial E}{\partial T}\right)_v \Delta T + \left(\frac{\partial E}{\partial V}\right)_T \Delta V$

Since $\qquad \Delta T = 0$, hence $\Delta E = \left(\frac{\partial E}{\partial V}\right)_T \Delta V = 0$

But $\qquad \Delta V \neq 0$, hence $\left(\frac{\partial E}{\partial V}\right)_T = 0$

That, is, the internal energy of a gas at constant temperature is independent of volume. It is strictly true for ideal gases. Again, at constant T, the pressure changes with volume, As E is independent of volume, it would be independent of pressure as well. Hence, $\left(\frac{\partial E}{\partial P}\right)_T = 0$

Hence thermodynamically, the ideal gases are required to satisfy,

$$\left(\frac{\partial E}{\partial V}\right)_T = \left(\frac{\partial E}{\partial P}\right)_T = 0 \qquad \ldots \text{(VIII.14)}$$

Moreover, we know ideal gases should obey Boyle's law, hence

$$\left[\frac{\partial(PV)}{\partial P}\right]_T = 0$$

8.13. Joule-Thomson Coefficient

Joule's experiment on free expansion of a gas into a vacuum,, just discussed, revealed that there would no temperature-change if the gas be ideal. But Joule and Thomson soon found that when a gas passes from a higher pressure to a lower one through fine orifices of a porous plug, there was usually a drop in temperature.

Suppose the volume V_1 of a gas under a constant pressure P_1 is allowed to pass through a porous barrier from the region on the left to the region on the right

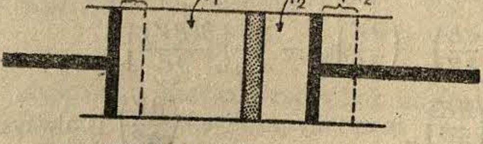


Fig. VIII.6. Joule-Thomson Expansion

where the constant pressure is P_2. The volume of the gas becomes V_2. The process is carried out with the slow motion of the two frictionlees pistons at the two ends (Fig. VIII.6). The whole system is thermally insulated, such that $q = 0$.

Now, the work done by piston on the left $= P_1V_1$
and the work obtained on the right $= P_2V_2$
Since $q = 0$, from the first law,

$$\triangle E = -w = P_1V_1 - P_2V_2$$

or $$E_2 - E_1 = P_1V_1 - P_2V_2$$

or $$E_2 + P_2V_2 = E_1 + P_1V_1$$

i.e. $$H_2 = H_1, \text{ or } \triangle H = 0$$

It shows that in the adiabatic expansion of a gas through fine orifices, the enthalpy remains constant. Such adiabatic expansions are also *isoenthalpic*. But in such cases, a drop in temperature of the outcoming gas is observed in most cases. This temperature-change is known as **Joule–Thomson effect.** The rate of change of temperature with pressure when enthalpy remains constant is called Joule-Thomson coefficient, (μ).

$$\mu = \left(\frac{\partial T}{\partial P}\right)_H \qquad \text{. . . (VIII.15)}$$

In such a flow the gas passes into lower pressures, hence dP is negative. Therefore μ is positive if dT is negative, *i.e.*, if temperature falls. At ordinary or lower temperatures, most gases cool down in passing to lower pressure through porous plugs. Hydrogen and Helium however become heated in such flow at room temperatures, *i.e.*, μ is negative. To explain:

$$H = f(P,T)$$

or $$dH = \left(\frac{\partial H}{\partial P}\right)_T dP + \left(\frac{\partial H}{\partial T}\right)_P dT$$

Since in *J-T* effect, $dH = 0$,

$$\therefore \quad \left(\frac{\partial H}{\partial T}\right)_P dT = -\left(\frac{\partial H}{\partial T}\right)_T dP$$

or $$\left(\frac{\partial T}{\partial P}\right)_H = -\left(\frac{\partial H}{\partial P}\right)_T \Big/ \left(\frac{\partial H}{\partial T}\right)_P = -\frac{1}{C_p}\left(\frac{\partial H}{\partial P}\right)_T$$

or $$\mu = -\frac{1}{C_p}\left(\frac{\partial H}{\partial P}\right)_T = -\frac{1}{C_p}\left(\frac{\partial E}{\partial P}\right)_T - \frac{1}{C_p}\left[\frac{\partial(PV)}{\partial P}\right]_T$$

For an ideal gas, both the terms on the rt-hand side separately vanish. Hence ideal gases have no Joule-Thomson effect.

J-T effect is appreciable with real gases. Rewriting, we have

$$\mu = -\frac{1}{C_p}\left(\frac{\partial E}{\partial V}\right)_T \left(\frac{\partial V}{\partial P}\right)_T - \frac{1}{C_p}\left[\frac{\partial(PV)}{\partial P}\right]_T \qquad \text{. . . (VIII.16)}$$

In this equation $\left(\frac{\partial E}{\partial V}\right)_T$ is usually positive, $\left(\frac{\partial V}{\partial P}\right)$ is always negative. Hence the first term is always positive. The quantity $\left[\frac{\partial(PV)}{\partial P}\right]_T$ is negative at low pressures and low temperatures. Under such conditions, the second term becomes positive; so μ is positive, *i.e.* there would be *J-T* cooling.

But at high pressures and at especially higher temperatures, $\left[\frac{\partial(PV)}{\partial P}\right]_T$ is positive. Hence, the second term becomes negative. If its value exceeds that of the 1st term, μ becomes negative. The *J-T* cooling effect is observed at relatively low temperatures. but if the temperature be high then instead of cooling the gases become heated (μ negative). Thus, for every gas there is a temperature where $\mu = 0$, when neither heating nor cooling of the gas would occur on passing through orifices to lower pressure. This is called the *inversion temperature* T_i of the gas.

For a Vander Waals gas, it has been shown that the $J-T$ coefficient can be expressed as,

$$\mu = \frac{1}{C_p}\left[\frac{2a}{RT} - b\right] \qquad \ldots\text{(VIII.17)}$$

At the inversion temperature T_i, $\mu = 0$;

$$\text{hence} \quad \frac{2a}{RT_i} - b = 0, \quad \text{or} \quad T_i = \frac{2a}{Rb} \qquad \ldots\text{(VIII.18)}$$

At high temperatures, $\frac{2a}{RT} < b$, hence μ is negative.

At low temperatures, $\frac{2a}{RT} > b$, hence μ is positive.

The importance of Joule-Thomson cooling has been observed in the liquefaction of gases.

At ordinary temperatures, for H_2 and *He*, the value of $2a/RT$ is quite small and less than b, hence μ is negative. So these gases get heated on passing through an orifice to lower pressures. But at extremely low temperature, $2a/RT > b$, and μ is positive. Hence at very low temperatures, H_2 and He also would cool on *J-T* expansion.

8.14. Adiabatic Processes in Ideal gases

An adiabatic change, by definition, is one which does not allow any transfer of heat; *i.e.*, $q = 0$. It follows from the 1st Law,

$$\triangle E = -w,$$

$$\text{for small changes,} \quad dE = -dw$$

If only mechanical work of expansion or contraction is involved, $dw = PdV$. Moreover, $dE = C_v dT$.

$$\therefore \quad C_v dT = -PdV$$

For a system of 1 mole of an *ideal* gas, expanding adiabatically from temp. T_1 to T_2 and volume V_1 to V_2, we have

$$C_v dT = -\frac{RT}{V}dV$$

$$\text{or} \quad \int_{T_1}^{T_2} C_v \frac{dT}{T} = -\int_{V_1}^{V_2} R\frac{dV}{V}$$

Integrating, $$C_v \ln \frac{T_2}{T_1} = -R \ln \frac{V_2}{V_1} = R \ln \frac{V_1}{V_2}$$

or $$\ln \frac{T_2}{T_1} = \ln \left(\frac{V_1}{V_2}\right)^{\frac{R}{C_v}} = \ln \left(\frac{V_1}{V_2}\right)^{\gamma-1} \quad ; \quad [\because R = C_p - C_v]$$

where γ = the heat-capacity ration C_p/C_v.

Hence, $$T_2 V_2^{\gamma-1} = T_1 V_1^{\gamma-1} = \text{constant}$$

i.e., $$TV^{\gamma-1} = \text{constant} \qquad \ldots \text{(VIII.19)}$$

Substituting T by $\frac{PV}{R}$, $$\frac{PV}{R} V^{\gamma-1} = \text{constant}$$

i.e., $$PV^{\gamma} = R \times \text{constant} = \text{constant} \qquad \ldots \text{(VIII.20)}$$

Similarly, $$TV^{\gamma-1} = T\left(\frac{RT}{P}\right)^{\gamma-1} = \text{constant}$$

or $$T^{\gamma} P^{1-\gamma} = \text{constant}/R^{\gamma-1} = \text{constant} \qquad \ldots \text{(VIII.21)}$$

Therefore, in adiabatic mechanical change of an ideal gas;

$$PV^{\gamma} = \text{constant}; T^{\gamma}P^{1-\gamma} = \text{constant and } TV^{\gamma-1} = \text{constant} \qquad \ldots \text{(VIII.22)}$$

For the adiabatic expansion of an ideal gas, $PV^{\gamma} = K'$

Also we know for isothermal expansion of the same, $PV = K$

The slope of the P-V curve will be obtained from $\frac{dP}{dV}$.

Adiabatic change; $P = K'/V^{\gamma}$; $$\frac{dP}{dV} = \frac{K'}{V^{\gamma+1}}(-\gamma) = -\gamma \frac{P}{V}$$

Isothermal change; $P = \frac{K}{V}$; $$\frac{dP}{dV} = -\frac{K}{V^2} = -\frac{P}{V}$$

In both the changes, the slope is negative. Since γ is greater than 1, the slope in the adiabatic P-V curve will be larger than that in the isothermal one (Fig. VIII.7).

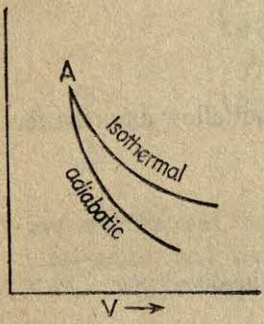


Fig. VIII.7

Adiabatic Work : (*i*) We have seen that in the adiabatic process, work

$$w_{ad} = -\triangle E$$

or $$w_{ad} = -C_v \triangle T = -C_v(T_2 - T_1) = C_v(T_1 - T_2) \qquad \ldots \text{(VIII.23)}$$

where T_1, T_2 are initial and final temperatures.

(*ii*) For 1 mole of gas, $T = PV/R$, hence adiabatic work,

$$w_{ad} = C_v\left(\frac{P_1V_1}{R} - \frac{P_2V_2}{R}\right) = \frac{C_v}{R}(P_1V_1 - P_2V_2)$$

$$= \frac{P_1V_1 - P_2V_2}{\gamma - 1} \qquad \ldots \text{(VIII.24)}$$

where P_1, V_1 are the initial and P_2, V_2 the final pressures and volumes.

Problem: A sample of a gas initially at 27°C is compressed from 40 litres to 4 litres adiabatically and reversibly. Calculate the final temperature ($C_v = 5$ cal/mole).

Assuming ideal behaviour, $C_p = C_v + 2 = 7$ cal/mole

$$\therefore \gamma = C_p/C_v = 7/5 = 1.4$$

If T be the final temp., then $\frac{T}{300} = \left(\frac{40}{4}\right)^{\gamma-1} = (10)^{0.4}$

$$\text{whence } T = 753.6°\text{K}$$

Problem: Ten litres of Helium expanded reversibly and adiabatically from 10 atm to 1 atmosphere. The final volume is 25 litres. Calculate the adiabatic work.

$$w_{ad} = \frac{P_1V_1-P_2V_2}{\gamma-1} = \frac{10\times10-25\times1}{1.66-1} = 113.6 \text{ litre-atmospheres. } (\gamma_{He} = 1.66)$$

EXERCISES

1. (*a*) State the 'law of conservation of energy' and explain it with examples. (*b*) what is *internal energy*? Can you quantitatively define its change?

2. Explain a thermodynamically reversible process. Show by an example that work from a reversible process would be maximum.

3. Find out, from the 1st Law, the thermodynamic criteria which would characterise (*i*) a cyclic process (*ii*) an adiabatic change and (*iii*) ideal gases.

4. What is Joule-Thomson effect? Show that sometimes gases would be heated from Joule-Thomson expansion. What is the effect of J-T expansion with ideal gases?

5. Derive mathematical expressions for
(*a*) Joule-Thomson coefficient
(*b*) Relation between C_p and C_v for an ideal gas. (Guru nanak Univ.)

6. Establish PV^{γ} = Constant for adiabatic processes with ideal gases.

7. Indicate the circumstances in which a gas on adiabatic expansion (*i*) may remain unaltered in temperature (*ii*) may be heated.

8. At 25°C, a quantity of air was compressed reversibly and adiabatically from 10 litres to 1 litre. Assuming ideal behaviour, calculate the final temperature ($\gamma = 1.4$). **[Ans: 476°C]**

9. 3 moles of oxygen occupied 75 litres at 1 atm. The pressure was raised to 100 atm reversibly and adiabatically. Find out its temperature and volume after compression ($C_v = 5$ cal/mole). **[Ans: 857°C; 2.788 litres]**

10. Write notes on: (*i*) adiabatic work (*ii*) inversion temperature (*iii*) heat content (*iv*) state functions.

11. Three moles of an ideal gas at 0°C was isothermally and reversibly expanded from 6.72 litres to 67.2 litres. Calculate the work. (Calcutta Univ.) **[Ans: 15.75 kJ]**

12. 15 moles of an ideal gas expands reversibly from 105 litres to 1050 litres at 27°C. How much heat would be absorbed in the process? (Cal. Univ.) **[Ans: 20727 Cal]**

13. One mole of water is vaporised at its normal boiling point. How much work would be involved? Sp. volume of water vapour = 1670 c.c./gm. **[Ans 3.06 kJ]**

14. 4.46 moles of an ideal gas ($C_v = 3/2$ R) at 0°C and 10 atm. pressure expanded until the pressure reduced to 1 atm. Calculate the Final volume and also the work obtained when the expansion was (*a*) isothermal and reversible (*b*) adiabatic and reversible and (*c*) when the pressure is suddenly reduced to 1 atm. **[Ans: (*a*) 100 lit, 2.331 kJ (*b*) 39.8 lit; 9.125 kJ (*c*) 5.47 kJ]**

15. Assuming nitrogen to be an ideal gas, calculate the work done by 20 gm nitrogen in expanding isothermally and reversibly from a volume of 10 litres to 20 litres at 27°C. What are q, ΔE and ΔH? (Calicut Univ.) [Ans: $\Delta E = 0$, $w = q = \Delta H = 297.2$ cal]

16. Calculate ΔH and ΔE if 10 litres of argon at N.T.P. inside a gas cylinder be heated to 100°C assuming ideal behaviour. [Ans: 223.1 cal, 133.8 cal]

17. Calculate the work involved when

(*i*) 45 gm ice melt into water at NTP. The volume decrease = 1.48 c.c./mole

(*ii*) One gm-atom of zinc dissolved in the anode of a Daniell cell (E = 1.1 volt)

(*iii*) 50 gm $CaCO_3$ decomposes at 327°C [Ans: (*i*) -3.7×10^{-3} lit-atm (*ii*) 212 kJ (*iii*) 600 cal

18. A system undergoes a change by two different paths. By 1st path, $w_1 = 0$, $q_1 = 20000$ cal. By the second path, $w_2 = 0.5\, w_{max}$ and $q_2 = 18000$ cal. If the change took place in reversible fashion, what would maximum work be? [Ans: 16.8 kJ]

CHAPTER 9

THERMOCHEMISTRY

9.1. Exothermic and Endothermic Reactions

All chemical reactions are usually accompanied with thermal changes; either heat is absorbed or heat is evolved during the chemical process.

An *exothermic reaction* is one in which heat is *evolved.*

An *endothermic reaction* is one in which heat is *absorbed.*

The heat of reaction is the amount of heat liberated or absorbed when the moles of reactants (*as given in the equation*) have completely been transformed into the products.

In the old system, the heat of reaction (q) was given along with the products in the chemical equation with a positive sign if heat is evolved or with a negative sign if heat is absorbed. For example,

$$C + O_2 \rightarrow CO_2 + 94300 \text{ cal (exothermic)}$$
$$H_2 + I_2 \rightarrow 2HI - 12680 \text{ cal (endothermic)}$$

At present, this method of expression is no longer followed.

Thermo Chemical Equations : Generally, the chemical reactions take place at constant pressure; the thermal change at constant pressure is q_p. But we know (eqn. VIII.10), $q_p = \triangle H$.

If the reaction occurs at constant volume, the heat-change is q_v. From (eqn. VIII.5), $q_v = \triangle E$.

In many reactions, q_p would differ from q_v. Now a-days, the thermal changes are expressed in terms of $\triangle H$ and $\triangle E$. The values of $\triangle H$ or $\triangle E$ are written on the right side of the equation. Following usual thermodynamic convention, $\triangle H$ (or $\triangle E$) would be negative if heat is liberated. If heat is absorbed $\triangle H$ (or $\triangle E$) would be positive. Thus,

$$C_7H_8 + 9O_2 = 7CO_2 + 4H_2O; \qquad q_p = \triangle H = -930 \text{ Kcal}$$
$$q_v = \triangle E = -928.8 \text{ Kcal}$$

Similarly,

Exothermic reactions: (i) $HCl + NaOH \rightarrow NaCl + H_2O$; $\triangle H = -13400$ cal
(ii) $C + O_2 \rightarrow CO_2$; $\triangle H = -94300$ cal
Endothermic reactions: (i) $N_2 + O_2 \rightarrow 2NO$; $\triangle H = +42000$ cal
(ii) $H_2 + I_2(g) \rightarrow 2HI$; $\triangle H = +11800$ cal

Retation between q_p and q_v

$$q_p = \triangle H_p = \triangle E_p + P\triangle V$$

where $\triangle V$ is the change in volume of the system in the chemical process.

Again $q_v = \triangle E_v$

$\therefore q_p - q_v = \triangle E_p - \triangle E_v + P\triangle V$

But the difference of $\triangle E_p$ and $\triangle E_v$ is negligible and in fact these are equal in the case of ideal gases. Hence, assuming $\triangle E_p = \triangle E_v$,

$$q_p = q_v + P\triangle V = q_v + P(V_2 - V_1) = q_v + n_2RT - n_1RT.$$

or
$$q_p = q_v + \triangle nRT \qquad \ldots \text{(IX.1)}$$

where $\triangle n$ = moles of resultants—moles of reactants.

In considering value of $\triangle n$, the solid or liquid participants are to be ignored.

Example: At 27°C, ammonia is synthesised as:

$$N_2 + 3H_2 \rightarrow 2\,NH_3\ ; \quad \triangle H = -23700 \text{ cal}$$

Calculate q_v for this reaction.

$$\triangle n = 2-4 = -2$$

$$q_v = q_p - \triangle nRT. = \triangle H - \triangle nRT = -23700-(-2) \times 2 \times 300$$
$$= -22500 \text{ cal.}$$

Example: The heat of combustion of liquid ethanol into CO_2 and H_2O is -327 Kcal at constant pressure at 27°C. Calculate q_v.

$$\underset{\text{liq}}{C_2H_5OH} + \underset{\text{gas}}{3O_2} \rightarrow \underset{\text{gas}}{2CO_2} + \underset{\text{liq}}{3H_2O};\quad \triangle H = -327 \text{ Kcal}$$

$$\triangle n = 2-3 = -1;\ q_v = q_p - \triangle nRT = -327-(-1) \times 2 \times 10^{-3} \times 300$$
$$= -326.4 \text{ Kcal}$$

Dependence of heat of reaction on the physical states: The heat-changes in chemical reactions also depend upon the physical state of the reactants and the resultants. The letters *g*, *l* and *s* written on the side of the formula would indicate its gaseous, liquid and solid state. To illustrate:

(1) $2C_6H_6\,(l) + 15O_2 \rightarrow 12CO_2 + 6H_2O(l);\qquad \triangle H = -981 \text{ Kcal}$
$\quad 2C_6H_6\,(g) + 15O_2 \rightarrow 12CO_2 + 6H_2O\,(l);\qquad \triangle H = -776 \text{ Kcal}$
(2) $C + 2S\,(s) \rightarrow CS_2\,(g);\qquad \triangle H = +25.4 \text{ Kcal}$
$\quad C + 2S\,(g) \rightarrow CS_2\,(g);\qquad \triangle H = -22.0 \text{ Kcal}$

When reactions occur in solutions, the heats of reaction depend on the concentration of the solutions. In very dilute solutions, the heats of reaction acquire a constant value. The symbol (*aq*) is written by the side of the formula to indicate very dilute state of the solution, e.g.,

$$H_2SO_4(aq) + 2NaOH(aq)) = Na_2SO_4(aq) + 2H_2O;\quad \triangle H = -27.2 \text{ Kcal}$$

9.2. The Laws of Thermochemistry

The thermal changes in chemical processes are governed by two general laws.

A. Law of Lavoisier and Laplace. This law states that *the heat-change accompanying a chemical process in one direction is equal in magnitude but opposite in sign, to that accompanying the same reaction in the reverse direction.* That is, heat evolved when water is formed from hydrogen and oxygen is exactly equal to the heat absorbed in the decomposition of water into the elements.

$$H_2(g) + \tfrac{1}{2}O_2\,(g) = H_2O(l);\qquad \triangle H = -\ 68300 \text{ cal}$$
$$H_2O(l) = H_2\,(g) + \tfrac{1}{2}O_2(g);\qquad \triangle H = +\ 68300 \text{ cal}$$

It is obvious from the First Law. Suppose two reactants A and B change first into C and D with heat evolution (q) and subsequently C and D react to produce back A and B in the initial state with heat absorbed (q'). According to the First Law, heat-content (H) or energy-content (E) of the initial A and B would again return to the same magnitude. As such the net heat-content change or energy-content change would be zero. Hence,

$$q + q' = 0 \quad \text{or} \quad q = -q'$$

i.e., heat-changes in the two directions must be equal in magnitude but opposite in sign.

B. Hess's Law of Constant Heat Summation. This law states that *for a given chemical process, the net heat-change* (q_p or q_v) *will be the same whether the process occurs in one or in several stages.*

To illustrate, carbon and oxygen can give directly carbon dioxide, or these can first form carbon monoxide which may then be oxidised to carbon dioxide. The net heat-changes in either case will be the same.

$$\begin{array}{lll}
(a) & C + O_2 = CO_2; & q_P = -94.05 \text{ Kcal} \\
(b) & C + \frac{1}{2}O_2 = CO; & q'_P = -26.42 \text{ Kcal} \\
 & CO + \frac{1}{2}O_2 = CO_2; & q''_P = -67.63 \text{ K cal} \\
\hline
 & C + O_2 = CO_2 & \text{It is seen, } q_P = q'_P + q''_P
\end{array}$$

In accordance with the First Law, if the initial and final states be fixed, the change in the heat-content or energy-content of a system *i.e.*, $\triangle H_p$ and $\triangle E_v$ would be independent of the path. Hence q_p and q_v will be independent of the path, *i.e.*, heat-change of a reaction will be the same whether the reaction takes place in a single step or in several steps.

To cite another example, the heat evolved in the oxidation of methane to carbon dioxide and water is the same whether the reaction occurs in one step or in several steps.

$$\begin{array}{lll}
\text{(I) } (a) & CH_4 + \frac{1}{2}O_2 \rightarrow CH_3OH; & \triangle H = -39.0 \text{ Kcal} \\
(b) & CH_3OH + \frac{1}{2}O_2 \rightarrow HCHO + H_2O; & \triangle H = -39.0 \text{ Kcal} \\
(c) & HCHO + \frac{1}{2}O_2 \rightarrow HCOOH; & \triangle H = -70.2 \text{ Kcal} \\
(d) & HCOOH + \frac{1}{2}O_2 \rightarrow CO_2 + H_2O; & \triangle H = -64.6 \text{ Kcal} \\
\hline
\text{Adding,} & CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O; & \triangle H = -212.8 \text{ Kcal}
\end{array}$$

On direct burning:

$$\text{(II) } CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O; \qquad \triangle H = -212.8 \text{ Kcal}$$

One singular advantage of this principle is that we can add or subtract the heat-changes in the process, as we have seen in the examples given above. In other words, the thermochemical equations may be treated algebraically. Some examples are given below.

Example: (*i*) The heats of oxidation of magnesium and iron are given:

$$\begin{array}{lll}
(a) & Mg + \frac{1}{2}O_2 = MgO; & \triangle H = -145700 \text{ cal} \\
(b) & 2Fe + \frac{3}{2}O_2 = Fe_2O_3; & \triangle H = -193500 \text{ cal}
\end{array}$$

Calculate the heat produced in the reaction: $3Mg + Fe_2O_3 = 3MgO + 2Fe$

Multiplying (*a*) by 3,

(*c*) $3Mg + \frac{3}{2}O_2 = 3MgO; \qquad \Delta H = -3 \times 145700 \text{ cal}$

and reversing (*b*),

(*d*) $Fe_2O_3 = 2Fe + \frac{3}{2}O_2; \qquad \Delta H = +193500 \text{ cal}$

Adding (*c*) and (*d*), $3Mg+Fe_2O_3 = 3MgO+2Fe; \; \Delta H = -243600 \text{ cal}$

Example (*ii*). Given (*a*) $2P + 3Cl_2 \rightarrow 2PCl_3; \qquad \Delta H = -151.8 \text{ Kcal}$

(*b*) $PCl_3 + Cl_2 \rightarrow PCl_5; \qquad \Delta H = -32.8 \text{ Kcal}$

Calculate the heat of formation of PCl_5, as

$$P + \tfrac{5}{2}Cl_2 \rightarrow PCl_5$$

Multiply (*a*) by $\frac{1}{2}$ and then add (*b*),

$$P + \tfrac{5}{2}Cl_2 \rightarrow PCl_5; \quad \Delta H = -\tfrac{1}{2}(151.8) - 32.8 = -108.7 \text{ Kcal}$$

The equations supplied have to be so arranged as to form the equation of the desired reaction.

9.3. Heat of Formation, ΔH_f^o

The thermal change occurring when one mole of a substance is formed from its constituent elements is called its *heat of formation*. When one mole HCl is produced from hydrogen and chlorine, 22.06 Kcal of heat is evolved. Hence heat of formation of HCl is −22.06 Kcal.

When heat is evolved in the formation of a compound from the elements, the compound is an *exothermic* one; if heat is absorbed the substance is called an *endothermic* compound.

The heat of formation is denoted by ΔH_f, the suffix 'f' indicating its formation from the elements.

Compound	ΔH_f (Kcal)	Compound	ΔH_f (Kcal)
$\frac{1}{2}H_2 + \frac{1}{2}Cl_2 \rightarrow HCl;$	−22.06	$\frac{1}{2}N_2 + \frac{1}{2}O_2 \rightarrow NO;$	+ 21.60
$\frac{1}{2}N_2 + \frac{3}{2}H_2 \rightarrow NH_3;$	−11.04	$2C + H_2 \rightarrow C_2H_2;$	+ 54.19

The heat of reaction at a constant pressure, q_p, is really the enthalpy-change of the process. It is therefore the difference of enthalpies of the products and the reactants.

$$q_p = \Delta H_{reaction} = H_{products} - H_{reactants} \qquad \text{. . . (IX.2)}$$

Now, suppose elements A and B unite to form the compound C,

$$A + B \rightarrow C$$

then the heat of formation of C would be

$$\Delta H_{f(c)} = H_c \text{-} (H_A + H_B)$$

Since enthalpy depends upon pressure and temperature. For thermochemical measurements, the standard condition chosen is 25°C and 1 atm. The standard enthalpy is H°, the superscript 'O' indicating standard state. Hence standard heat of formation ΔH_f° is given by,

$$\Delta H_f^o = H_C^o - H_A^o - H_B^o$$

When the element exists in several allotropic forms, the enthalpy of the stable variety is taken for the standard; thus graphite is taken for carbon, rhombic sulphur for sulphur.

The heats of reaction involve only differences in enthalpy, hence the absolute enthalpy-contents of the products and reactants are of no consequence, provided the same scale of measurement is used always. The molar enthalpy of the element in the standard state has been arbitrarily defined to be *zero*. Thus, at 1 atm and 298°K, carbon (graphite), oxygen, sodium, mercury, etc., all have *zero* enthalpy. Hence,

$$\triangle H_f^o = H_c^o - H_A^o - H_B^o = H_c^o\,, \quad [\because H_A^o = H_B^o = 0]$$

$$\therefore \triangle H_f^o = H_c^o \qquad \ldots \text{(IX.3)}$$

∴ *The standard enthalpy of a compound = its standard heat of formation*

For any general reaction; P + Q → R + S

$$\begin{aligned}\triangle \mathrm{H}^o_{reaction} &= H_r^o + H_s^o - H_p^o - H_q^o \\ &= \triangle H^o_{f(R)} + \triangle H^o_{f(s)} - \triangle H^o_{f(p)} - \triangle H^o_{f(Q)} \\ &= \triangle H^o_{f(products)} - \triangle H^o_{f(reactants)}\end{aligned}$$

Hence heat of reaction can be computed form the heats of formation of the participating species.

Example: Calculate the heat of oxidation of ethyl alcohol to carbon dioxide, when the heats of formation of carbon dioxide and liquid water are given as −94.05 and −68.32 K cal. The heat of formation of ethyl alcohol is −66.4 Kcal

$$\begin{array}{lllll} & C_2H_5OH(l) + 3O_2 & = 2CO_2 + & & 3H_2O(l) \\ \triangle H^\circ_f & -66.4 & \quad 0 & 2\times(-94.05) & 3\times(-68.32) \end{array}$$

$$\begin{aligned}\therefore \quad \triangle H &= 2\triangle H^\circ_{f(CO_2)} + 3\triangle H^\circ_{f(H_2O)} - 3\triangle H^\circ_{f(alc)} - 3\triangle H^\circ_{f(O_2)} \\ &= 2(-94.05) + 3(-68.32) - (-66.4) - 3\times 0 \\ &= -326.6 \text{ Kcal}\end{aligned}$$

That is, 326.6 Kcal heat will be evolved in the oxidation of ethanol.

The knowledge of heat of reaction along with other heats of formation would enable the computation of a desired heat of formation.

Example: For the reaction,

$$CO + NO = \tfrac{1}{2}N_2 + CO_2; \qquad \triangle H^\circ = -374 \text{ kJ}$$

Find out the heat of formation of CO, if $\triangle H^\circ_{f(NO)} = +90.2$ kJ and $\triangle H^\circ_{f(CO_2)} = -394$ kJ

Now, $\triangle H^\circ = \frac{1}{2}\triangle H^\circ_{f(N_2)} + \triangle H^\circ_{f(CO_2)} - \triangle H^\circ_{f(CO)} - \triangle H^\circ_{f(NO)}$

or $-374 = \frac{1}{2}\times 0 + (-394) - (90.2) - \triangle H^\circ_{f(CO)}$

or $\triangle H^\circ_{f(CO)} = -110.2$ kJ

Example: The heats of formation of CO_2 from diamond and graphite are

−94500 and −94050 cal respectively. What is the enthalpy-change in the transformation of diamond to graphite?

$$\begin{array}{lrcll} & C_{dia} + O_2 & = & CO_2; & \triangle H_1^\circ = -94500 \text{ cal} \\ & C_{gra} + O_2 & = & CO_2; & \triangle H_2^\circ = -94050 \text{ cal} \\ \text{Subtracting,} & C_{dia} & = & C_{gra}; & \triangle H^\circ = -450 \text{ cal} \end{array}$$

Thus, the enthalpy change of transition can be evaluated from heats of formation. The heat content of graphite is thus less than that of diamond. Thus heat of transition can be computed from the heats of formation.

A few standard heats of formation have been assembled in the Table here:

TABLE: STANDARD HEATS OF FORMATION AT 25°C IN KCAL/MOLE

Substance	$\triangle H^\circ_f$	*Substance*	$\triangle H^\circ_f$
$H_2O(g)$	− 57.79	Na_2O (s)	− 99.4
H_2O (l)	− 68.32	CuO (s)	− 37.10
HCl (g)	− 22.06	PbO (s)	− 52.5
HBr (g)	− 6.83	ZnO (s)	− 83.17
HI (g)	+ 6.33	Al_2O_3 (s)	− 399.09
N_2O (g)	+ 19.49	CaO (s)	− 151.90
NO (g)	+ 21.6	NaCl (s)	− 98.23
CO (g)	− 26.42	KCl (s)	− 104.17
CO_2 (g)	− 94.05	CH_4 (g)	− 17.89
SO_2 (g)	− 70.9	C_2H_6 (g)	− 20.24
NH_3 (g)	− 11.04	C_2H_4 (g)	+ 12.50
HNO_3 (l)	− 41.4	C_2H_2 (g)	+ 54.19
H_2S (g)	− 5.3	C_6H_6 (l)	+ 11.70
NaOH (s)	− 102.00	CH_3OH (l)	− 57.02
KOH (s)	− 102.00	C_2H_5OH (l)	− 66.36

Heat of Formation of Ions: The thermal-change involved in the formation of an ion from neutral atom is the heat of formation of the ion. In this case, the heat of formation of H^+ ions in aqueous medium is taken as zero, *i.e.*, $\triangle H^\circ_{f(H^+)\,aq} = 0$ The heats of formation for other ions can then be easily obtained.

$$\begin{array}{lcccl} \text{For example,} & H^+ + & OH^- & \rightarrow \; H_2O; & \triangle H = -13360 \text{ cal} \\ & \triangle H^\circ_{f(H^+)} & \triangle H^\circ_{f(OH^-)} & \triangle H^\circ_{f(H_2O)} & \\ & o & x & -68320 \text{ cal} & \end{array}$$

$$\therefore \; \triangle H^\circ_{f(H_2O)} - x = -13360$$

$$\triangle H^\circ_{f(OH^-)} = x = -68320 + 13360 = -54960 \text{ cal}$$

Heats of formation of some ions are

Ions:	OH^-	Cl^-	SO_4^{--}	Na^+	Ba^{++}	
$\triangle H^\circ_f$ (Kcal):	−54.96	−40.02	−216	−57.28	−128.5	etc.

These data are useful in estimating the heats of formation of salts.

9.4. Heat of Combustion

The heat-change accompanying the complete combustion of a gm-mole of the substance at a given temperature under normal pressure is called its *heat of combustion*.

In estimating heat of combustion, the substance must be allowed to be oxidised to its final state. In the case of organic compounds, complete combustion is regarded to have taken place when these are transformed finally into CO_2 and H_2O. A few data for heats of combustion are given below.

TABLE: HEATS OF COMBUSTION AT 25°C IN KCAL

Compounds	ΔH	*Compounds*	ΔH
Methane	− 212.8	Methanol (*l*)	− 173.6
Ethane	− 372.8	Ethanol (*l*)	− 326.7
Ethylene	− 337.2	Cane sugar (*s*)	− 1349.0
Acetylene	− 310.6	Phenol (*s*)	− 732.0
Benzene (*l*)	− 780.9	Aniline (*l*)	− 812.0
Naphthalene (*s*)	− 1228.2	Benzoic acid (*s*)	− 771.4

The heat of combustion is usually determined in a 'bomb-calorimeter' internally enamelled with platinum and capable of withstanding high pressure (Fig. IX.1). It has a capacity of about 400 c.c. and is fitted with pressure-tight screw-cap. A weighed sample is placed in a cup inside and the bomb is filled with oxygen at 25−30 atm. The bomb is kept immersed in water in a calorimeter. When the system acquires a constant temp T_1, the reaction is initiated by passing a small electric current through the thin pt-wire dipped in the sample. The reaction produces a large amount of heat and the temperature-rise is accurately determined. In a separate control experiment, the products plus calorimeter are raised from T_1 to T_2 by electric heating, and the amount of electric energy used *Eit* is measured in the usual way. Evidently this energy (*Eit*) is equivalent to the heat produced during combustion. Remembering that the reaction occurred at constant volume,

$$q_v = -Eit$$

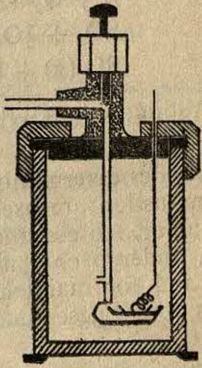


Fig. IX.1. bomb calorimeter

The experimentally determined heats of combustion are quite useful in evaluation of *heats of formation.*

Example: Calculate the heat of formation of ammonia. The heats of combustion of ammonia and hydrogen are −90.6 and −68.3 Kcal respectively.

Given (1) $2NH_3 + 3O = N_2 + 3H_2O$; $\Delta H = -2 \times 90.6 = -181.2$

(2) $H_2 + O = H_2O$; $\Delta H = -68.3$

or (3) $3H_2 + 3O = 3H_2O$; $\Delta H = -3 \times 68.3$

Subtracting (3) from (1) and re-arranging

$$2NH_3 = N_2 + 3H_2; \quad \Delta H = -181.2 + 3 \times 68.3 = +23.7$$

i.e., (4) $N_2 + 3H_2 = 2NH_3$; $\Delta H = -23.7$

Hence, heat of formation of ammonia, $\Delta H_f = -11.8$ Kcal

The heats of combustion are also often utilised in determining the heat of other reactions.

Example: Estimate the heat evolved in the reaction:

$$C_2H_5OH + O_2 = CH_3COOH + H_2O$$

when the heats of combustion of ethyl alcohol and of acetic acid are 325.1 Kcal and 209.5 Kcal respectively.

Now, (*a*) $C_2H_5(OH) + 3O_2 = 2CO_2 + 3H_2O; \quad \Delta H = -325.1$ Kcal

(*b*) $CH_3COOH + 2O_2 = 2CO_2 + 2H_2O; \quad \Delta H = -209.5$ Kcal

Subtracting (*b*) from (*a*) and rearranging:

$C_2H_5OH + O_2 = CH_3COOH + H_2O; \quad \Delta H = -325.1-(-209.5)$
$= -115.6$ K cal.

∴ The heat of the reaction is −115.6 Kcal

The heats of combustion are also useful in estimating the heat of formation of a compound in which the elements would not directly combine to produce the substance.

For example, the heat of formation of H_2SO_4 can be computed from the following data.

$H_2 + \frac{1}{2}O_2 \rightarrow H_2O\,(l); \quad \Delta H = -68.32$ Kcal
$S + O_2 \rightarrow SO_2; \quad \Delta H = -70.96$ Kcal
$SO_2 + \frac{1}{2}O_2 \rightarrow SO_3(g); \quad \Delta H = -23.49$ Kcal
$SO_3(g) + H_2O(l) \rightarrow H_2SO_4(l); \quad \Delta H = -31.14$ K cal

Adding $S + 2O_2 + H_2 \rightarrow H_2SO_4(l); \quad \Delta H = -193.91$ Kcal

Besides determining the heats of formation and of reactions, the data of heat of combustion are used in (*a*) estimating the calorific value of fuels like coke, gasoline etc, so essential for engineers (*b*) estimating the calorific values of food which undergo combustion in our system and supply the energy for mascular work and for maintenance of body temperature (*c*) assessing temperature of flames where gases undergo combustion.

9.5. Thermoneutrality of Solutions of salts

No thermal-change is observed when dilute solutions of inorganic salts of strong acids and strong bases are mixed. This is often called *thermoneutrality of salt solutions*. for example, $NaNO_3 + KCl \rightarrow NaCl + KNO_3; \ \Delta H = 0$

This is due to the fact that being salts of strong acids and bases, both the salts remain completely dissociated in solution. In mixing no change of ions would occur and hence no thermal-change.

$$Na^+ + NO_3^- + K^+ + Cl^-(aq) = Na^+ + Cl^- + K^+ + NO_3^-\,(aq); \ \Delta H = 0$$

But if the two solutions react to form a precipitate, there shall always be evolution of heat.

9.6. Heat of Neutralisation

All acid-base neutralisation reactions are exothermic. The amount of heat liberated when one gm-eqv. of an acid is neutralised by one gm-eqv. of base is called the *heat of netralisation*.

It has been found that when acid and base are both strong, the heat of neutralisation is always the same and is equal to 13.7 Kcal. This is because strong acids and bases remain completely dissociated in solution. For example:

(*i*) $HCl + NaOH \rightarrow NaCl + H_2O$
or $H^+ + Cl^- + Na^+ + OH^- \rightarrow Na^+ + Cl^- + H_2O$
or $H^+ + OH^- \rightarrow H_2O$

(*ii*) $\frac{1}{2}H_2SO_4 + KOH \rightarrow \frac{1}{2}K_2SO_4 + H_2O$
or $H^+ + \frac{1}{2}SO_4^{--} + K^+ + OH^- \rightarrow K^+ + \frac{1}{2}SO_4^{--} + H_2O$
or $H^+ + OH^- \rightarrow H_2O$

This means that neutralisation in every case really means the formation of a mole of water from H^+ and OH^- ions. Since the reaction is the same hence heat of neutralisation is the same.

But when a weak acid or a weak base is neutralised the heat of neutralisation in much less. For example,

$$NH_4OH + HCl \rightarrow NH_4Cl + H_2O; \qquad \triangle H = -12.3 \text{ Kcal}$$
$$HCN + NaOH \rightarrow NaCN + H_2O; \qquad \triangle H = -2.9 \text{ Kcal}$$

This is because the weak acid or base is very slightly dissociated and an appreciable portion of energy is uitlised in the process of dissociation of the weak counterpart. The heat of dissociation of the weak acid or base can be easily estimated. Suppose the weak acid HCN is neutralised by NaOH solution.

(*a*) $HCN\,(aq) + OH^-\,(aq) = CN^- + H_2O; \quad \triangle H = -2.9$ Kcal

But (*b*) $H^+(aq) + OH^-(aq) = H_2O; \quad \triangle H = -13.7$ Kcal

Subtracting (*b*) from (*a*) and rearranging,

$$HCN\,(aq) = H^+ + CN^-; \triangle H = -2.9 + 13.7 = +10.8 \text{ Kcal}$$

That is, HCN absorbs 10.8 Kcal for dissociation per mole.

9.7. Methods for determination of heat of reaction

Different methods are employed in the determination of the heat of reaction.

(*a*) *Calorimetry*: The heat of neutralisation, combustion, solution etc. are measured directly from calorimetric estimations.

(*b*) *Spectroscopy*: The heats of dissociation are very accurately computed from molecular spectra.

(*c*) *From thermochemical data*: We have already seen in the previous section how the heats of combustion and of formation are utilised in estimating the heat of reaction.

(*d*) *From Reaction isochore*: The variation of equilibrium constant with temperature is given by $\frac{dlnK}{dT} = \frac{\triangle H}{RT^2}$, where $\triangle H$ is the heat of reaction. The value of $\triangle H$ can be obtained by measuring eqm. constant at different temperatures. (see chapter on equilibrium).

9.8. Heat of Solution : Heat of Dilution

Normally the solution of a substance in a solvent is accompanied with thermal changes. *The heat-change produced when* 1 *mole dissolves in a solvent to give a solution of a definite concentration is called the 'integral heat of solution'*. It tends to a constant value at very dilute solution.

The heat-change of solution changes with concentration, e.g.;

$$NaCl\,(s) + 10H_2O \rightarrow NaCl(10H_2O), \qquad \triangle H = 490 \text{ cal}$$

$$NaCl(s) + 100H_2O \rightarrow NaCl(100H_2O); \qquad \triangle H = 1200 \text{ cal}$$

Since the heat of solution changes with concentration, there must be thermal changes when a concentrated solution is diluted with the same solvent.

The '*integral heat of dilution' is the thermal change which occurs when a solution containing* 1 *mole solute is diluted from a given concentration to another concentration.* Thus

$$HCl\,(g) + 10H_2O \rightarrow HCl(10H_2O); \qquad \triangle H = -17300 \text{ cal}$$

$$HCl\,(g) + 50H_2O \rightarrow HCl\,(50H_2O); \qquad \triangle H = -17500 \text{ cal}$$

∴ Heat of dilution,

$$HCl(10H_2O) + 40H_2O \rightarrow HCl(50H_2O); \qquad \triangle H = -200 \text{ cal}$$

Suppose 1 mole of the solute is added to a very large volume of its solution at a definite concentration, such that the change in concentration is negligible. The heat-change in such a process is called the '*differential heat of solution*'.

9.9. Influence of Temperature on Heat of Reaction: Kirchhoff's Equation

Suppose a reaction, X → Y, takes place at a constant pressure. The heat of reaction, $\triangle H$ is the difference of the enthalpies of X and Y, *i.e.* the heat-contents of products and reactants.

$$\triangle H = H_y - H_x$$

Differentiating with respect to temperature at constant pressure,

$$\left[\frac{\partial(\triangle H)}{\partial T}\right]_P = \left(\frac{\partial H_y}{\partial T}\right)_P - \left(\frac{\partial H_x}{\partial T}\right)_P$$

But $\left(\frac{\partial H_y}{\partial T}\right)_P = C_{p'y)}$ and $\left(\frac{\partial H_x}{\partial T}\right)_P = C_{p(x)}$

Hence $\left[\frac{\partial(\triangle H)}{\partial T}\right]_P = C_{p(y)} - C_{p(x)} = \triangle C_p$

where $\triangle C_p$ = difference of heat-capacities of products and reactants

Integrating between two temperatures T_2 and T_1,

$$\triangle H_2 - \triangle H_1 = \triangle C_p \int_{T_1}^{T_2} dT = \triangle C_p\,(T_2 - T_1)$$

assuming ΔC_p does not vary with temperature. This is known as *Kirchhoff's equation.* It permits computation of heat of reaction at any temperature from a knowledge of the same at another temperature.

Example: At 25°C, the heat of formation of liquid water is −68.32 Kcal. What will be the value at 100°C? Given C_p-values of $H_2(g)$, $O_2(g)$, $H_2O(l)$ as 6.89, 6.97 and 18 cal per degree respectively.

$$H_2(g) + \tfrac{1}{2}O_2(g) = H_2O(l); \qquad \Delta H = -68.32 \text{ Kcal}$$

$$\therefore \; \Delta C_p = 18-(6.89+\tfrac{1}{2}\times 6.97) = 7.63 \text{ cal} = 7.63 \times 10^{-3} \text{ Kcal}$$

$$\therefore \; \Delta H_{100°C} = \Delta H_{25°C} + \Delta C_p(T_2-T_1) = -68.32 + 7.63 \times 10^{-3} \times 75$$

$$= -67.748 \text{ Kcal}$$

9.10. Heat of Atomisation

The 'standard state' of an element is the state in which the element exists at 25°C and 1 atm. The heat required to produce 1 mole of atoms in the gaseous atomic state from the element in its standard state is called the *heat of atomisation.* These are often determined spectroscopically.

A few accepted values of the heats of atomisation are given here.

TABLE: HEAT OF ATOMISATION IN KCAL

Element	*Atomisation*	*Heat of atomisation (Kcal)*
Carbon	$C(s, gr) \rightarrow C(g)$	170.6
Hydrogen	$\tfrac{1}{2}H_2(g) \rightarrow H(g)$	52.1
Oxygen	$\tfrac{1}{2}O_2(g) \rightarrow O(g)$	59.6
Nitrogen	$\tfrac{1}{2}N_2(g) \rightarrow N(g)$	113.0
Chlorine	$\tfrac{1}{2}Cl_2(g) \rightarrow Cl(g)$	28.9

9.11. Bond Energy

The amount of energy required to separate an atom by breaking a bond with another atom is called the 'dissociation energy' Q_D of that bond. It depends on the nature of the atoms linked by the bond.

$$H{-}O{-}H \rightarrow H{-}O + H; \qquad Q_D^{O-H} = +120 \text{ Kcal}$$

To break the remaining bond of OH-group,

$$H{-}O \rightarrow H + O; \qquad Q_D^{O-H} = +101 \text{ Kcal}$$

The average value of the dissociation energies of a given bond in a series of a similar dissociating species is called the *bond-energy* of that bond-type.

Thus, the bond-energy of the O—H bond would be

$$\Delta H_B^{O-H} = \tfrac{1}{2}(120 + 101) \text{ Kcal} = 110.5 \text{ Kcal}$$

This is supported from the fact that when 1 mole H_2O breaks up into H_2 and $\tfrac{1}{2}O_2$, the heat required is + 110 Kcal.

Similarly the bond-energy of a C—H bond can be obtained from the energies of dissociation of the four bonds of methane. The complete dissociation of a mole of methane needs 397 Kcal.

Hence, the bond-energy of C$-$H bond $= \frac{1}{4} \times 397 = 99$Kcal. Some of the accepted values of bond-energies are given here.

TABLE: BOND ENERGIES IN KCAL

Bond	*Energy*	*Bond*	*Energy*
C $-$ C	83.1	H $-$ H	103.2
C $=$ C	140	O $-$ O	33
C $\equiv$ C	198	O $=$ O	118
C $-$ H	99	Cl $-$ Cl	57.8
C $-$ O	84	Br $-$ Br	46
C $=$ O	173	I $-$ I	36
C $-$ Cl	78.5	N $\equiv$ N	225
C $-$ N	69.7	O $-$ H	110.5
N $-$ H	93.4	Cl $-$ H	103
C $-$ Br	66	O $-$ Cl	49

Determination of Bond-energy: The bond-energy is often computed from the heats of atomisation and heat of formation. The bond-energy of a C—C bond can be obtained as follows:

The heat of formation of ethane is -20.3 Kcal;

$$2C(s) + 3H_2(g) \rightarrow C_2H_6(g); \qquad \triangle H_f = -20.3$$

Reversing; (*a*) $C_2H_6(g) \rightarrow 2C(s) + 3H_2(g); \qquad \triangle H = +20.3$

Again, (*b*) $2C(s) \rightarrow 2C(g); \qquad \triangle H_a = +(2 \times 170.9)$

(*c*) $3H_2(g) \rightarrow 6H(g); \qquad \triangle H_a = +(6 \times 52.1)$

Adding (*a*), (*b*) and (*c*),

$$C_2H_6(g) \rightarrow 2C(g) + 6H(g); \quad \triangle H = 20.3 + 2 \times 170.9 + 6 \times 52.1$$
$$= 674.7 \text{ Kcal}$$

That is, the energy of breaking one C—C bond and six C—H bonds is 674.7 Kcal. The bond-energy of a C—H bond is 99 Kcal.

$\therefore$ Bond-energy of a C—C bond $= 674.7 - 6 \times 99 \approx 81$ Kcal

Estimation of heat of reaction from bond-energies: The heat of reaction of the chlorination of ethane can be obtained as follows.

$$C_2H_6 + Cl_2 \rightarrow C_2H_5Cl + HCl$$

The bond-energies of reactants and products are as follows.

Reactant	$\triangle H_B$(Kcal)	Products	$\triangle H_B$ (Kcal)
1 C$-$H	98	1 C$-$Cl	78
1 Cl$-$Cl	57	1 H$-$Cl	102
	155		180

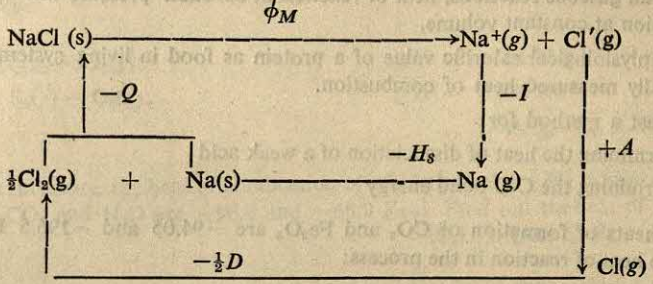
The bonds of C_2H_5 radical being common on both sides need not be considered.

Hence the heat of reaction, $\triangle H = 155 - 180 = -25$ Kcal

Born-Haber Cycle. The lattice energy of an ionic crystal is really the energy of the reaction,

$$MX(s) \rightarrow M^+(g) + X^-(g)$$

This energy cannot be directly measured. It is evaluated by conceiving a series of operations completing a cyclic process. We may illustrate this with the sodium chloride crystals. The cyclic process, called *Born-Haber Cycle*, may be schematically represented as.



where ϕ_M = lattice energy
H_S = heat of sublimation of *Na*
D = heat of dissociation of Cl_2
I = ionisation potential of *Na*
A = electron affinity of chlorine
Q = heat of formation of NaCl

Starting with a gm-mole of NaCl crystal, the process consists of converting it into gaseous Na^+ and Cl^- ions and subsequently reuniting the ions to produce back the solid NaCl. The steps in the complete cycle are as follows:

Processes	Energy-changes
(*a*) $NaCl(s) \rightarrow Na^+(g) + Cl^-(g)$	ϕ_M
(*b*) $Na^+ + \epsilon = Na;\ Cl^- - \epsilon = Cl$	$-I + A$
(*c*) $Cl \rightarrow \frac{1}{2}Cl_2$	$-\frac{1}{2}D$
(*d*) $Na(g) \rightarrow Na(s)$	$-H_s$
(*e*) $Na(s) + \frac{1}{2}Cl_2 \rightarrow NaCl(s)$	$-Q$

The cycle is completed at a constant temperature, hence

$$\phi_M - I + A - \tfrac{1}{2}D - H_s - Q = 0$$

$$\text{or}\quad \phi_M = Q + H_s + \tfrac{1}{2}D + I - A$$

The quantities on the right-hand side are measurable, some from spectroscopy and *A* from electron emission expt. Hence, the lattice energy ϕ_M is known.

EXERCISES

1. State Hess's Law and illustrate with an example.

2. Explain with examples: (*a*) Heat of combustion (*b*) Enthalpy-change of formation (*c*) Heat of solution (*d*) endothermic reactions and (*e*) bond-energy.

3. "The standard enthalpy of a compound is the same as its standard heat of formation." —Justify.

4. Define 'heat of Combustion'. Describe an experimental method for its determination. Mention some uses of the data of the heat of combustion.

5. Show that (*i*) $q_p = q_v + \Delta n\ RT$ for gaseous reactions
(*ii*) The heat of neutralisation of a strong base with a strong acid should always be the same.

6. Correct or Justify the following statements giving reasons.

(*a*) Allotropic modifications of an element on combustion will liberate the same amount of heat

(*b*) The heat of solution will be the same whether the solute is added in big crystals or in finely powdered state

(*c*) The heat of formation of $H_2O\ (g)$ will be larger than that of $H_2O\ (l)$

(*d*) For all gaseous reactions, heat of reaction at constant pressure will be greater than the heat of reaction at constant volume.

(*e*) The plysiological calorific value of a protein as food in living systems is less that its calorimetrically measured heat of combustion.

7. Suggest a method for

(*i*) determining the heat of dissociation of a weak acid

(*ii*) determining the C-C bond energy

8. The heats of formation of CO_2 and Fe_2O_3 are −94.05 and −196.5 Kcal respectively. Calculate the heat of reaction in the process:

$$2C\ (s) + 2\ Fe_2O_3\ (s) \rightarrow 4Fe\ (s) + 3\ CO_2\ (g)$$

[Ans: $\Delta H\ = 110.8$ Kcal]

9. The enthalpies of formation of the following are known in kilojoules.

CO	H_2O	C_2H_2	N_2O
−110.5	−241.8	+ 226.7	+ 82.05 kj

Estimate the heat of reaction of the process:

$$C_2H_2 + 3N_2O \rightarrow 2CO + H_2O + 3N_2$$

[Ans: $\Delta H_f = -935.7$ kj]

10. Compute the heat of formation of benzene from the following: The heats of formation of water and CO_2 are −68.0 and −94.05 Kcal respectively. The heat of combustion of benzene is −799.3 Kcal [Ans. $\Delta H_f = 31$ Kcal]

11. Calculate the heat of formation of methane from the following:

$C\ (graph) + O_2(g) \rightarrow CO_2;$ $\Delta H = -94.1$ Kcal

$H_2\ (g) + \frac{1}{2}\ O_2\ (g) \rightarrow H_2O\ (l);$ $\Delta H = -68.3$ Kcal

$CH_4\ (g) + 2O_2\ (g) \rightarrow CO_2\ (g) + 2H_2O\ (l);$ $\Delta H = -212.8$ Kcal

(Punjab Univ.) [Ans: —18 Kcal]

12. Given the heats of atomisation,

$C\ (graph) \rightarrow C\ (g)\ ;$ $\Delta H = +\ 172$ Kcal

$H_2\ (g) \rightarrow 2H\ (g)\ ;$ $\Delta H = +\ 104$ Kcal

and the heat of formation,

$C\ (graph) + 4H\ (g) \rightarrow CH_4\ (g);$ $\Delta H = -\ 18$ Kcal

Find out the bond-energy of a C—H bond.

13. Find out the heat of formation of Al_2Cl_6 form the following data:

$Al\ (s) + 3HCl\ (aq) \rightarrow AlCl_3 + \frac{3}{2}\ H_2\ (g)$ $\Delta H = -127$ Kcal

$H_2(g) + Cl_2\ (g) \rightarrow 2HCl(g)$ $\Delta H = -44$ Kcal

$HCl(g) + aq \rightarrow HCl\ (aq)$ $\Delta H = -17.5$ Kcal

$Al_2Cl_6\ (s) + aq \rightarrow 2AlCl_3(aq)$ $\Delta H = -155.8$ Kcal

(Vikram Univ.) [Ans: $\Delta H_f = -335.2$ Kcal]

14. Assess the heat of formation of NaOH. Given

$Na(s) + H_2O(l) + aq \rightarrow NaOH(aq) + \frac{1}{2}H_2(g)$, $\Delta H = -43.8$ Kcal

$H_2(g) + \frac{1}{2}O_2(l) \rightarrow H_2O(l)$; $\Delta H = -68.4$ Kcal

$NaOH(s) + aq \rightarrow NaOH(aq)$; $\Delta H = -10.3$ Kcal

[Ans: $\Delta H_f = -101.9$ Kcal]

15. Calculate the heat of transition of monoclimic sulphur to rhombic sulphur at room temperature. Given:

$S_\beta(s) + O_2(g) \rightarrow SO_2(g)$; $\Delta H = -71030$ cal

$SO_2(g) \rightarrow S_\alpha(s) + O_2(g)$; $\Delta H = 70960$ cal

[Ans. $S_\beta \rightarrow S_\alpha$, $\Delta H = -70$ cal]

16. At const. pressure, the heat of combustion of ethyl alcohol is -341.8 Kcal and the heats of formation of CO_2 and H_2O are -96.0 and -68.0 Kcal. Find out the heat of formation of ethyl alcohol. (C.U.) [Ans. $\Delta H_f = -54.2$ Kcal]

17. The heats of combustion of ethane and ethylene are -368.4 and -331.6 Kcal. The heat of formation of water is -68.4 Kcal. Find the heat of transformation of ethane to ethylene. (C.U.) [Ans. $\Delta H = +31.6$ Kcal]

18. From the following heats of formation,

$2C(s) + 3H_2(g) \rightarrow C_2H_6(g)$; $\Delta H_f = -20236$ cal

$2C(s) + 3H_2(g) + \frac{1}{2}O_2 \rightarrow C_2H_5OH(l)$; $\Delta H_f = -66356$ cal

Calculate ΔH for the reaction,

$C_2H_6(g) + \frac{1}{2}O_2 \rightarrow C_2H_5OH(l)$; (Kerala Univ.) [Ans. $\Delta H = -46120$ cal]

19. When 1 mole water at 100°C is converted into steam at 1 atm, 9720 cal heat are absorbed. The molar volumes of water and steam are 18 c.c. and 30600 c.c. respectively. Calculate ΔE of the process. (Kurukshetra Univ.) [Ans. 8978 cal]

20. At 17°C, calculate the heat of polymerisation of acetylene into benzene at constant pressure, when the heats of the following reactions are given at constant volume:

(*i*) $2C(s) + O_2(g) \rightarrow CO_2(g)$; $\Delta H = -96960$ cal

(*ii*) $2H_2(g) + O_2(g) \rightarrow 2H_2O(l)$; $\Delta H = -136720$ cal

(*iii*) $2C_6H_6(l) + 15O_2(g) \rightarrow 12CO_2(g) + 6H_2O(l)$; $\Delta H = -1598700$ cal

(*iv*) $2C_2H_2(g) + 5O_2(g) \rightarrow 4CO_2(g) + 2H_2O(l)$; $\Delta H = -620100$ cal

(Bombay Univ.) [Ans. $\Delta H = -131960$ cal]

21. Evaluate the heat of formation of $SO_3(g)$ From the following data,

$PbO(s) + S(s) + \frac{3}{2}O_2(g) = PbSO_4(s)$; $\Delta H = -165.6$ Kcal

$PbO(s) + H_2SO_4.5H_2O(l) \rightarrow PbSO_4(s) + 6H_2O(l)$; $\Delta H = -23.3$ Kcal

$SO_3(g) + 6H_2O(l) \rightarrow H_2SO_4.5H_2O(l)$; $\Delta H = -41.1$ Kcal

(C. U.) [Ans. $\Delta H_f = -101.2$ Kcal]

22. At 18°C, $C + CO_2 \rightarrow 2CO$; $\Delta H = -41.950$ Kcal

The C_p-values of C, CO_2 and CO are 2.496, 9.066 and 6.791 cal/mole. Calculate the heat of reaction at 50°C. [Ans. $\Delta H = -42015$ cal]

23. The standard heat of formation of HBr (g) is −8600 cal. Calculate the same at 250°C. The C_p-values of hydrogen, bromine and hydrogen bromide are 3.41, 0.055 and 0.086 cal/°C. [Ans. −52250 cal]

24. Evaluate the heat of reaction for the process,

$$CH_4(g) + Cl_2(g) \rightarrow CH_3Cl(g) + HCl\,(g)$$

using bond-energy values from the Table. [Ans. $\triangle H = -24$ Kcal]

25. The heat of ionisation of water is + 13.6 Kcal. The heat of neutralisation of NH_4OH by HCl is −12.3 Kcal. Find out the heat of dissociation of NH_4OH. [Ans. 1300 cal]

26. A solution of composition $CuCl_2 + 10H_2O$ is diluted with x moles of water, the heat disengaged is given by $Q_V = \frac{x \times 5023}{x + 21.24}$. The heat of solution of $CuCl_2$ in 600 moles of water is 11080 calories. Find out the heat of solution of anhydrous $CuCl_2$ in 10 moles of water. What heat would be evolved if a solution $CuCl_2 + 600\ H_2O$ be infinitely diluted? (C. U.) [Ans. 173 cal]

27. The heat of formation of ethylene is + 12.4 Kcal. The heats of atomisation of carbon and hydrogen are 170.9 Kcal and 52.1 Kcal respectively. The C−H bond energy is 99 Kcal. Estimate the C = C bond-energy. [Ans. 141 Kcal]

CHAPTER 10

THE SECOND LAW OF THERMODYNAMICS

10.1. The need for the Second Law

The First Law merely tells us that during a change or transformation of energy an equivalence in their quantities are maintained. But there is an element of incompleteness in the First Law. This law does not indicate whether a change would at all occur and, if it occurs, to what extent and in which direction.

To illustrate: (*a*) Suppose two bodies A and B are brought in contact. From the first law, we only know that if q calories of heat are lost by A, exactly q calories of heat would be gained by B, or *vice versa.* But the law does not state if A would lose heat or B. To know the direction of flow of heat we need an additional information, namely the temperatures of A and B.

(*b*) Consider the chemical change, $PCl_5 \rightleftharpoons PCl_3 + Cl_2$: the first law merely tells us that if Z calories of heat be evolved in dissociation of PCl_5, exactly Z calories would be absorbed in the combination of PCl_3 and Cl_2. But if we have an arbitrary mixture of the three, PCl_5, PCl_3 and Cl_2, we cannot ascertain from the first law alone if there would be dissociation of PCl_5 or not. So, to ascertain in which direction the change would take place we need the knowledge of the equilibrium constant of the process.

These examples show the insufficiency of the First Law. To foretell the direction of a chemical or a physical process and to what extent the change would occur we need some more information or knowledge of some other criteria beyond the First Law. This is provided by the second Law.

10.2. Spontaneous Processes

The changes which take place automatically in a system without the aid of any external agency are termed *spontaneous processes.*

(*i*) Water from the Himalayas flows down the slopes till it reaches the Indian ocean (*ii*) A hot body loses heat to a colder body till the two reach an equilibrium temperature (*iii*) when a concentrated solution is mixed with a dilute one diffusion starts and continues until the concentration at every point is the same (*iv*) A gas will automatically pass into a region of low pressure or a vacuum, and so on.

Innumerable such natural processes are spontaneous. The spontaneous processes are *unidirectional, i.e.* take place in one direction and are *irreversible.* The changes do not occur spontaneously in the opposite direction. Water will not go up the slopes by itself; a dilute solution will not revert by itselt into a concentrated solution and a more dilute one.

In order to reverse the spontaneous changes, always outside effort would be required. To take water to the higher level, to concentrate the dilute solution, to take the gas back to higher pressure, external work has to be performed.

These experiences led to the statement:

All spontaneous processes are irreversible and always proceed towards equilibrium. This indeed is a qualitative expression of the second law since it suggests the direction of the change. Every natural process moves towards the equilibrium state.

During the spontaneous processes, seldom any useful work is obtained. Mostly the energy is transformed into heat. Only by introduction of suitable mechanisms, it is possible to obtain useful work from a spontaneous change. Thus, the flow of water downward would yield work if a turbine is installed, the spontaneous flow of heat from higher to lower temperature produces work if a heat engine be employed, the movement of gas from a higher to a lower pressure would give work through a wind-mill.

10.3. The Second Law of Thermodynamics

Ever since men began to delve into the problem of producing more and more work, human ingenuity was exercised in converting heat into utmost work. This is because heat sources are common and it is readily available. But it is human experience that when every form of energy including mechanical work has a natural tendency to be transformed into heat, the latter, by itself, is never transformed into any other form. Only through some mechanism or machine can heat be converted into other forms; even then this conversion occurs only partially.

We have also another experience with heat energy. *Heat of, itself, will not pass from a lower to a higher temperature.* Or, as more elegantly stated by Clausius, *It is impossible for a self-acting machine, unaided by an external agency, to convey heat from a body at a low to one at a high temperature.* It suggests that work performed by external agency only would convey heat from lower to higher temperatures. It therefore covers an aspect of the second law.

The guidance as to the conditions under which heat changes into the direction of work would obviously come under the Second Law. For this reason, in enunciating the Second Law we often find the statements refer to the conversion of heat into work. It is now known that two conditions must be fulfilled to utilise heat for useful work.

1. A contrivance or mechanism, commonly called the 'thermodynamic engine', is essential. Without the aid of an engine the conversion of heat into work is impossible. Further, the engine must work in a reversible cyclic process.

2. The engine must operate between two temperatures. It will take up heat at a higher temperature, convert a portion of it into work and give up the rest of the heat to a body at lower temperature.

We have seen in Sec 8.8, if an ideal gas expands isothermally and reversibly, the heat (q) absorbed from the surrounding is rendered wholly into work, $q = w = RT \ln V_2/V_1$. But in such complete conversion, the external agency (cylinder-system) has suffered a change in volume from V_1 to V_2. That is, *complete conversion of heat into work is impossible without making a permanent change somewhere,* To repeat the same conversion again, the ideal gas must come back to its original volume, in which work equal to $RT \ln \frac{V_2}{V_1}$ has to be done on the system by the surroundings. The net result is that the engine working in a cycle at a temperature same as that of the source would yield *no work*. It is a fact of experience that *under isothermal conditions no engine can convert heat into work.*

All attempts to produce work by taking up heat continuously from a reservoir and gradually cooling it have failed. This is known as *perpetual motion of the second kind.* An engine carrying perpetual motion of the second kind could never be constructed. Ostwald said; *It is impossible to construct a perpetual motion machine of the second kind.* That is why our buses or cars cannot be run with heat from the surrounding air or we cannot utilise the vast amounts of ocean heat to move our ships.

The second law has been stated by summarizing these experiences as:

(*i*) *It is impossible by an inanimate material agency* (*an engine*) *to derive mechanical effect* (*work*) *from any portion of matter by cooling it below the temperature of the coldest of the surroundings* (*Kelvin*).

(*ii*) *It is impossible to construct an engine, working in a cycle which would produce no effect except the raising of a weight and the cooling of a heat reservoir* (*Planck*).

The statement of Planck is the same as that of Ostwald regarding perpetual motion of the second kind. Kelvin's statement urges that heat from low temperature source would not yield work.

The quantitative aspect of this experience, that is how much of a quantity of heat can be converted into work was explained first clearly by Sadi Carnot.

10.4. The Carnot Cycle

Carnot started with two essential pre-requisites. Firstly, to estimate the work obtained from heat during its passage from a higher to a lower temperature, the external agency (the engine) must come back to its original state so as to exclude any work involved in its own change. That is, the engine must operate in complete cycles. Secondly, to obtain maximum work in a cycle of operations, every step should be carried out in a reversible fashion.

The typical Carnot cycle consists of four successive operations using one gm-mole of a perfect gas as the working substance. We take the gas enclosed in a cylinder fitted with a frictionless piston. To start with, the cylinder containing the gas is kept in a large thermostat at the higher temperature T (source) and suppose the volume of the gas be V_1.

Operation 1. The gas is allowed to expand isothermally and reversibly from the volume V_1 to the volume V_2.

The heat absorbed by the gas = Q (say),

The work done by the gas = $RT \ln \frac{V_2}{V_1}$,

Since the gas is ideal, we know, $Q = RT \ln \frac{V_2}{V_1}$ ...(X.1)

Operation 2. The cylinder is next taken out of the thermostat and kept in a thermally insulated enclosure. The gas is allowed to expand further from volume V_2 to volume V_3 adiabatically and reversibly until the temperature falls down to that of the sink T'.

The heat absorbed by the gas = nil

The work done by the gas $= C_V(T-T')$; (see eqn. VIII.23)

Operation 3. The cylinder is then placed in a thermostat at temperature T' (sink); the gas is compressed isothermally and reversibly until the volume changes to V_4, from V_3.

The heat given out by the gas $= Q'$ (say)

The work done by the gas $= RT' \ln \frac{V_4}{V_3}$

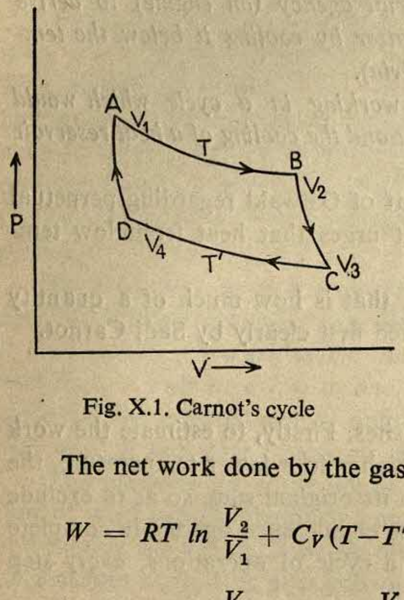


Fig. X.1. Carnot's cycle

[Since V_4 is smaller than V_3, the work is negative which means work is done *on* the gas]

Operation 4. The cylinder is now thermally isolated as in operation 2. The gas is then adiabatically and reversibly compressed to its initial volume V_1 and its original temperature T is attained. The gas thus comes back to its initial state.

The heat absorbed by the gas = nil

The work done by the gas $= C_V(T'-T)$

These operations may be represented by a *P-V* diagram as in Fig. X.1. The total area enclosed within *ABCD* would represent the work obtained in the cyclic process.

The net work done by the gas in the complete cycle,

$$W = RT \ln \frac{V_2}{V_1} + C_V(T-T') + RT' \ln \frac{V_4}{V_3} + C_V(T'-T)$$

$$= RT \ln \frac{V_2}{V_1} - RT' \ln \frac{V_3}{V_4}$$

But considering the adiabatic changes in operations 2 and 4, we have from eqn. VIII.22,

$$(a)\ TV_2^{\gamma-1} = T'V_3^{\gamma-1}$$

and

$$(b)\ TV_1^{\gamma-1} = T'V_4^{\gamma-1}$$

dividing,

$$\frac{V_2}{V_1} = \frac{V_3}{V_4}$$

$$\therefore\ W = RT \ln \frac{V_2}{V_1} - RT' \ln \frac{V_2}{V_1} = R(T-T') \ln \frac{V_2}{V_1}$$

The efficiency (η) of the process is given by the ratio of W and Q.

$$\eta = \frac{W}{Q} = \frac{R(T-T')\, ln\, \frac{V_2}{V_1}}{RT\, ln \frac{V_2}{V_1}} = \frac{T-T'}{T} = 1 - \frac{T'}{T} \qquad \ldots (X.2)$$

$$\text{and} \quad W = Q\frac{T-T'}{T} = Q\,\frac{\triangle T}{T} \qquad \ldots (X.3)$$

This relation expresses the maximum amount of work obtainable from the heat flowing from T to T'. This is the mathematical form of the Second Law.

Notes: (*a*) Only $\triangle T/T$ fraction of the total quantity of heat taken from the source can be transformed into work.

(*b*) From equation X.2, the efficiency of the engine depends only on the temperatures of the source and the sink. It is independent of the working substance of the engine provided the engine is reversible. All reversible engines are equally efficient between the same working temperatures. It can also be shown that an irreversible engine would be less efficient than a reversible one.

(*c*) The efficiency would be 1, when the whole of heat Q is rendered into work. This is possible only when $T' = 0$°K. Since this is not practically realisable, hence η is always less than 1.

(*d*) When $T = T'$, $\eta = 0$. It means engine cannot produce any work by operating under *isothermal* conditions.

Problem: The available heat from a source is 8000 cal. A reversible engine works between b.pt. of water and 30°C. Calculate the work done, efficiency and the heat rejected to the sink.

$$\text{Efficiency,} \quad \eta = \frac{T-T'}{T} = \frac{373-303}{373} = 0.19 \text{ or } 19\%$$

$$\text{Work done, } w = Q\,\frac{\triangle T}{T} = 8000 \times 0.19 = 1520 \text{ cal} = 6.38 \text{ kJ}$$

$$\text{Heat rejected to sink, } Q_2 = Q_1 - w = 8000 - 1520 = 6480 \text{ cal}$$

10.5. Concept of Entropy

It is now necessary to introduce a new thermodynamic function called *entropy*, which is closely related to the second law. For a specified change of a system, the thermal change q (or dq for infinitesimal changes) will have different values depending upon the path of transformation. This means q is not a state function; its value cannot be obtained only from the initial and final parameters of the system. We generally say, dq is not a perfect differential.

Surprisingly, although dq-value depends upon the path of transformation, the value of $\frac{dq_r}{T}$, *i.e.*, the ratio of the reversible thermal-change and temperature is found to be independent of the path. It means that if $\frac{dq_r}{T}$ at all stages of the transformation be summed up, the net value would be the same irrespective of the manner of transformation of the system; the changes should be reversible ones. This may be illustrated from the familiar Carnot cycle.

Consider a Carnot cycle as represented in Fig. X.2 in which *ab* and *cd* are the isothermals at temperatures T_1 and T_2; *bc* and *da* are the adiabatic stages. Let dq_1 be the heat supplied to the working system at T_1 and dq_2 be the heat rejected by it to the sink at T_2. All steps are *reversible.* We know, in a Carnot cycle,

$$\frac{dq_1-dq_2}{dq_1}=\frac{T_1-T_2}{T_1} \text{ or } \frac{dq_1}{T_1}=\frac{dq_2}{T_2} \qquad \ldots(\text{X.4})$$

(dq_2 is negative as it is rejected by the system.)

Now let us confine our attention only to the change of the system from the point *a* to the point *c* and attempt to find out the ratio of the heat-change to the temperature at which the thermal change occurs. We can proceed from *a* to *c* either along *abc* or along *adc.*

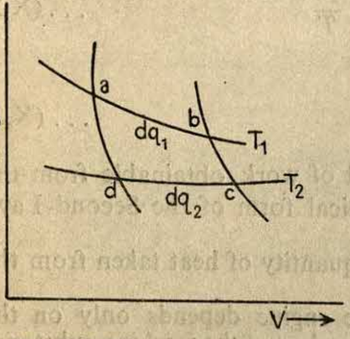


Fig. X.2. The Carnot's cycle

Along the path *abc*, we have the isothermal *ab*, when heat-change dq_1 takes place at T_1, followed by adiabatic change *bc* having no heat-change. Hence,

$$\frac{\text{heat-change}}{\text{temp.}}=\frac{dq_1}{T_1}+0=\frac{dq_1}{T_1}$$

Along the path *adc*, the adiabatic *ad* involves no thermal change, but along the isothermal *dc*, remembering *reversibility,* heat absorbed would be dq_2 at temperature T_2. Hence,

$$\frac{\text{heat-change}}{\text{temp.}}=0+\frac{dq_2}{T_2}=\frac{dq_2}{T_2}$$

But $$\frac{dq_1}{T_1}=\frac{dq_2}{T_2}$$

That is, the ratio of the heat-change to temperature, dq/T is the same whatever path might be followed by the system in its *reversible* change. Hence, we say, dq_r/T is a perfect differential, the suffix *r* indicating reversiblity.

Moreover, if we consider the four steps of the entire Carnot cycle, the sum of dq_r/T-values would be,

$$\sum\frac{dq_r}{T}=\frac{dq_1}{T_1}+0-\frac{dq_2}{T_2}+0=\frac{dq_1}{T_1}-\frac{dq_2}{T_2}$$

In a Carnot cycle, $\frac{dq_1}{T_1}=\frac{dq_2}{T_2}$, hence $\sum\frac{dq_r}{T}=0$

or, $$\oint\frac{dq_r}{T}=0 \qquad \ldots(\text{X.5})$$

This applies to all reversible cyclic processes.

10.6. Definition of Entropy

The heat-change *dq* and the temperature *T* are thermodynamic quantities. Therefore, we can say that the system has a thermodynamic function whose change, measured by $\frac{dq_r}{T}$, is independent of the path of the transformation of the system. This function has been called *entropy* by Clausius and is denoted by the symbol S. Its change dS is measured by the ratio of the reversible heat-change and the temperature at which the heat-change occurs, *i.e.*,

$$dS = \frac{dq_r}{T}, \quad \text{or} \quad TdS = dq_r \qquad \ldots (X.6)$$

the suffix r indicating reversibility.

We can now say:

(*i*) *Entropy S is a thermodynamic state function. Its magnitude would depend upon the parameters (P, V, T) only of the system.*

(*ii*) *The entropy change dS is independent of the path of transformation. Its value depends upon the initial and final states of the system. dS is always given by* $dq_{\text{rev.}}/T$.

(*iii*) *Absorption of heat increases the entropy of the system. Rejection of heat leads to a decrease in its entropy.*

(*iv*) *In a reversible adiabatic change,* $dq = 0$. *These are isoentropic changes.*

(*v*) *Entropy is an extensive property, it increases with increase in mass of the system. The entropy is expressed in units of calories/°K, called entropy units (e.u.).*

Since entropy is a function of state only, the entropy-change of a system from a given state I to a given state II is always the same and is independent of the path. Only if the path is reversible, we know the change in entropy will be given by,

$$\triangle S = S_{II} - S_I = \int_I^{II} dq_r/T \qquad \ldots (X.7)$$

Hence in order to compute the entropy-change of a system in an irreversible process, we may conceive of taking the system from state I to state II along any *reversible* path and then divide the heat absorbed at each point by the temperature and sum up the quotients.

In a reversible cyclic process, $\oint \frac{dq_r}{T} = \oint dS = 0$

From the first law in a cyclic process, $\oint dE = 0$

10.7. Entropy Change of the Universe

When a system absorbs heat its entropy increases. The same amount of heat is lost by the surroundings and its entropy decreases. The sum of the entropy-changes of the system and the surroundings together is called the entropy of the universe.

$$\triangle S_{\text{univ.}} = \triangle S_{\text{system}} + \triangle S_{\text{surr.}}$$

We may consider some typical cases now.

(*a*) *Reversible Process*: Consider the reversible isothermal expansion of an ideal gas as in *ab* of step I of the Carnot cycle (Fig. X.2). Here, the gain in entropy of the gas $= q_r/T$

the loss in entropy of the surroundings $= \dfrac{q_r}{T}$

The net change in entropy, $\triangle S_{\text{univ.}} = 0$

In all reversible processes, the net entropy-change $= 0$

We have seen that the entropy-change of the Carnot cycle is nil (eqn. X.5). In this cyclic process, the heat-changes of the surroundings are opposite to those of the system but equal in magnitude. Hence in the Carnot cycle, $\triangle S_{\text{surr.}} = 0$.

In all cyclic process, the net entropy-change,

$$\triangle S_{\text{univ.}} = \triangle S_{\text{system}} + \triangle S_{\text{surr.}} = 0 + 0 = 0$$

(*b*) *Irreversible Process*: In all irreversible processes, there is always an increase in net entropy. Let us illustrate.

(*i*) *Irreversible flow of heat.* Suppose a heat-reservoir at temp. T_1 is brought in contact with a second reservoir at a lower temp. T_2. Let a small quantity of heat q flow from T_1 to T_2.

The decrease in entropy of $A = \dfrac{q}{T_1}$, the increase in entropy of $B = \dfrac{q}{T_2}$

$$\therefore \quad \text{net entropy-change} = \frac{q}{T_2} - \frac{q}{T_1} = q.\frac{T_1 - T_2}{T_1 T_2} = +\,ve \text{ quantity}$$

Hence, irreversible flow of heat leads to an increase in entropy.

(*ii*) *Irreversible isothermal expansion of an ideal gas.* Suppose n moles of an ideal gas be enclosed in a vessel A of volume v_1. The vessel is connected through a stop-cock to a completely evacuated vessel B of volume v_2. The temperature is T and the system is insulated (Fig. X.3).

If the stop-cock is opened, the gas would spontaneously irreversibly expand to the volume $v_1 + v_2$. The work w is zero, and the heat supplied (q) from surroundings is zero. Hence $\triangle E$ is zero and temperature remains unaltered.

$$q = \triangle E + w = 0$$

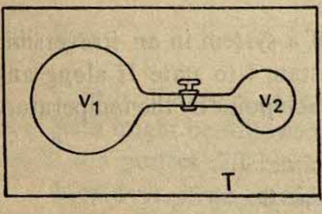


Fig. X.3

Now if this expansion of the gas were carried out reversibly at T°K from volume v_1 to volume $(v_1 + v_2)$, the heat absorbed,

$$q_{\text{rev}} = \triangle E + RT\,ln\,\frac{v_1 + v_2}{v_1} = 0 + RT\,ln\,\frac{v_1 + v_2}{v_1}$$

$$\therefore \qquad \triangle S_{\text{system}} = \frac{q_{\text{rev}}}{T} = R\,ln\,\frac{v_1 + v_2}{v_1}$$

Since dS is a perfect differential, $\triangle S_{\text{irr}}$ (system) would be the same. The surroundings has no thermal-change, hence $\triangle S_{\text{surr}} = 0$

Hence in the irreversible expansion of the gas,

$$\triangle S_{\text{univ}} = \triangle S_{\text{sys}} + \triangle S_{\text{surr}} = R\,ln\,\frac{v_1 + v_2}{v_1} + 0 = R\,ln\,\frac{v_1 + v_2}{v_1} = +\,ve$$

It may be categorically stated that in any irreversible process, there would be a net increase in entropy.

In nature, the processes occurring spontaneously are all irreversible. Therefore, broadly speaking the spontaneous changes in nature would always cause entropy-increase. Thus, the fall of an apple from a tree, the flowing of a river downhill, the rusting of iron, the mixing of two gases and so on, are all spontaneous and irreversible changes and these would lead to an increase in entropy. In other words, a natural process will take place in a direction in which the net entropy would increase; or, a process which would not raise the entropy of the universe, will not spontaneously occur. However, in all such changes the energy may be transformed but the total quantity remains constant. This is why the two laws of thermodynamics are often stated as,

(*a*) First Law : *The net energy of the universe remains constant.*

(*b*) Second Law: *The net entropy of the universe tends to a maximum.*

Clausius Inequality: Whether a system changes reversibly or irreversibly, $\triangle E$ for a given transformation will always be the same. Hence,

$$\triangle E = (q-w)_{\text{rev}} = (q-w)_{\text{irr}}$$

But we know, $w_{\text{rev}} > w_{\text{irr}}$, hence,

$$q_{\text{rev}} > q_{\text{irr}}, \quad \text{or} \quad dq_{\text{rev}} > dq_{\text{irr}}$$

But $dq_{\text{rev}} = TdS$, therefore $TdS > dq_{\text{irr}}$

$$\text{or} \quad dS > \frac{dq_{\text{irr}}}{T}$$

This is known as the 'Clausius Principle of Inequality'.

10.8. Entropy and Available Work

Suppose we have two heat reservoirs A and B at temperatures T_1 and T_2, such that $T_1 > T_2$. A third reservoir is the sink C at a much lower temperature T. Let Q calories of heat be supplied to a reversible engine working between A and C, then the available work,

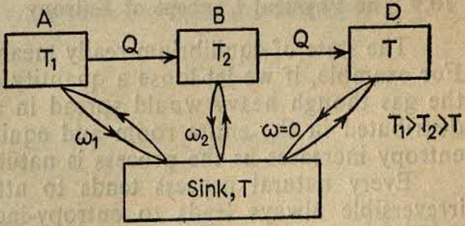


Fig. X. 4

$$w_1 = Q.\frac{T_1-T}{T_1} = Q\left[1 - \frac{T}{T_1}\right]$$

If we allow this heat (Q) to flow from A to B first and then supplied to the engine to work between B and C, then the available work,

$$w_2 = Q\left[1 - \frac{T}{T_2}\right]$$

So, $$w_1 - w_2 = Q\left[\frac{T}{T_2} - \frac{T}{T_1}\right] = T.Q\,\frac{T_1-T_2}{T_1T_2} = + \text{ ve quantity.}$$

It means $w_2 < w_1$, the available work from the same heat supply has decreased due to the irreversible flow of heat from T_1 to T_2. The amount of work *unavailable* (ϕ) is,

$$\phi = w_1 - w_2 = T.Q\,\frac{\triangle T}{T_1T_2}$$

By the irreversible flow of heat from A to B, the entropy-increases and

$$\triangle S = \frac{Q}{T_2} - \frac{Q}{T_1} = Q \cdot \frac{\triangle T}{T_1 T_2}$$

Hence, unavailable work, $\phi = TQ \cdot \frac{\triangle T}{T_1 T_2} = T \triangle S$

Hence with increase in entropy, ϕ (unavailable work) will increase. Or, with increase in entropy the availability of work diminishes.

Suppose now, the same heat (Q) flows to a reservoir D, whose temperature is T, the same as that of the sink. The available work, $w_D = Q\left(1 - \frac{T}{T}\right) = 0$. No work is available; ϕ has reached its maximum. Therefore the entropy has increased to its maximum. Under conditions of equilibrium, for any minute virtual change, $dS = 0$. Entropy thus determines the condition of the system as to its capability of yielding work.

In a spontaneous change, S increases; $\triangle S > 0$

At the equilibrium state, S is maximum; $\triangle S = 0$

In a non-spontaneous change, S decreases; $\triangle S < 0$

10.9 The Physical Concept of Entropy

The state of equilibrium really means a state of maximum disorder or chaos. For example, if we let loose a quantity of yellowish green chlorine in this room, the gas though heavy would spread in all directions until it is most chaotically distributed in the entire room and equilibrium is attained. In this diffusion the entropy increases as the process is natural, irreversible and spontaneous.

Every natural process tends to attain equilibrium. These processes being irreversible always leads to entropy-increase. The more a system approaches equilibrium, the greater is the disorder and irreversibility. When equilibrium is reached, the system has the maximum disorder. The entropy goes on increasing and reaches its maximum value at the equilibrium state. In other words, the entropy is a *measure of the disorder* of the system or it may be called the extent of *mixed-up-ness* of the system.

When a liquid vaporises it absorbs heat; the entropy increases and simultaneously chaotic motion of the molecules increases.

We have also seen that at equilibrium the system can no more yield work. We say, the system is run down. The more the system is run down the greater becomes the entropy. At equilibrium, the system is completely run down and the entropy is maximum. The entropy has been considered by Tolman as a measure of the rundown-ness of a system.

10.10. Entropy Relations

The relation between entropy and internal energy or enthalpy would be

$$dE = dq - w = TdS - PdV \qquad \ldots \text{(X.8)}$$

and $$dH = dE + PdV + VdP = TdS + VdP \qquad \ldots \text{(X.9)}$$

Entropy-change with temperature: Since S is a state function, we may express entropy as $S = f(V, T)$

or
$$dS = \left(\frac{\partial S}{\partial T}\right)_V dT + \left(\frac{\partial S}{\partial V}\right)_T dV$$

At constant volume, $dS_V = \left(\frac{\partial S}{\partial T}\right)_V dT = \frac{1}{T}\left(\frac{T\partial S}{\partial T}\right)_V dT = \frac{C_V}{T} dT$

Integrating, $$\triangle S_V = \int_{T_1}^{T_2} C_V \, dlnT = C_V ln \frac{T_2}{T_1} \qquad \ldots (X.10)$$

where C_V is the heat-capacity of the system at constant volume.

Likewise at a constant pressure, $\triangle S_P = C_P ln \frac{T_2}{T_1}$ . . . (X.11)

Problem: Calculate $\triangle S$ when 20 gm Argon is heated from 27°C to 227°C at constant pressure.

20 gm Argon = 0.5 mole; C_P = 5.0 cal/mole (monatomic)

$$\triangle S = C_P \, ln \frac{T_2}{T_1} = 0.5 \times 5 \times 2.303 \log (500/300) = 1.275 \text{ e.u.}$$

10.11. Entropy of an Ideal Gas

It is possible to express the entropy of a *perfect gas* now from the first law,

$$dq = dE + PdV$$

Dividing both sides by T,

$$\frac{dq}{T} = \frac{dE}{T} + \frac{PdV}{T} = C_V \frac{dT}{T} + R \frac{dV}{V}, \quad \text{(for 1 gm-mole)}$$

or $$dS = C_V \, d \, lnT + R \, d \, lnV$$

or $$S = C_V \, lnT + R \, lnV + S_0 \qquad \ldots (X.12)$$

[where S_0 is a constant; heat-capacities assumed to remain unaltered.]

Integrating (X.12) between the temperatures T_1 and T_2 and volumes V_1 and V_2,

$$\triangle S = C_V \, ln \frac{T_2}{T_1} + R \, ln \frac{V_2}{V_1}$$

For an isothermalc hange; $\triangle S_T = R \, ln \frac{V_2}{V_1} = R \, ln \frac{P_1}{P_2}$ . . . (X.13)

Problem: What would be the entropy-change when 10 moles of an ideal gas be doubled in volume isothermally?

$$\triangle S = 10R \, ln \, v_2/v_1 = 10 \times 2 \times 2.303 \log 2 = 13.86 \text{ e.u.}$$

10.12. The Third Law and Entropy

We have seen that entropy is a measure of the disorder in a system. Conversely if order is restored, the entropy decreases. When a liquid freezes, the molecules become more orderly arranged. And in freezing the liquid loses heat and decreases in its entropy. With decrease in temperature, disorder gradually diminishes and hence entropy also gradually decreases.

If a pure substance be taken in the vicinity of absolute zero of temperature (0°K), it would be in crystalline form with the most perfect order and it should have the least entropy. Lewis and Randall stated, from various other considerations as well, that

Every system has a finite positive entropy and at absolute zero of temperature the entropy may become zero and does so become in the case of a pure crystalline substance. This is known as the third law of thermodynamics.

From eqn. (X.11), $dS = C_P \frac{dT}{T}$

Integrating between the temperatures T°K and 0°K,

$$S_T - S_0 = \int_0^T C_P \frac{dT}{T}$$

Since at 0°K, $S_0 = 0$, hence, entropy at the temperature T,

$$S_T = \int_0^T C_P \frac{dT}{T} = \int_0^T 2.303\, C_P \, d \log T$$

This equation enables the evaluation of entropy of a substance. (C_P) is plotted against log T commencing from very low temperature to the given temperature. The area under the curve would be a measure of the value of the entropy S_T (Fig. X. 5).

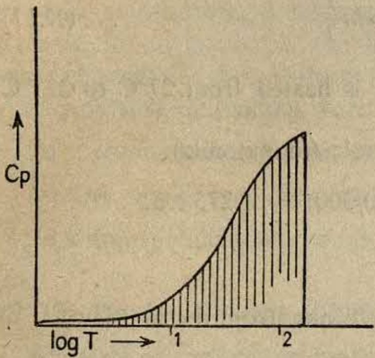


Fig. X. 5. Detn. of entropy

EXERCISES

1. Make any two formal statements for the Second law and show that both of them express the same basic fact.

2. Derive a quantitative expression for the Second law with the help of Carnot cycle. Will the efficiency of the reversible engine change if a real gas is used?

3. On what does the efficiency of an engine depend in the conversion of heat into work? Will the efficiency of an engine working between the same temperature limits increase if larger amount of heat be supplied from the source?

4. Deduce an expression for the efficiency of a reversible engine and from the expression develop the concept of entropy.

5. Write explanatory notes on: (*a*) Clausius inequality (*b*) Zeroth law of thermodynamics (*c*) Irreversible processes and entropy-change (*d*) Spontaneous Processes.

6. Define the Second Law in terms of entropy and prove it in the case of an isothermal irreversible expansion of an ideal gas. (Punjab Univ.)

7. Explain and define the term 'entropy'. What are its units? Arrive at the conclusion that the entropy of the universe is increasing. (Punjabi Univ.)

8. What is meant by 'entropy' of a system? What does it indicate regarding the properties of the system? Give an idea about its physical significance.

9. Deduce an experssion for the entropy of a mole of an ideal gas. What is the isothermal entropy-change if it expands from a pressure P_1 to P_2?

10. (*a*) All adiabatic changes are isoentropic

(*b*) No entropy-change would occur in adiabatic mixing of two ideal gases, as no heat enters into or escape from the system. Comment on these statements.

11. State the Third Law of thermodynamics. Give the outline of the principle for determining the entropy of a pure substance.

12. A Carnot engine working between 0°C and 100°C takes up 840 joules from the high temperature reservoir. Calculate the work done, heat rejected to the sink and the efficiency.

[Ans. $w = 0.225$ kJ, $Q' = 146$ cal, $\eta = 26.8\%$]

13. Calculate the entropy-change in :

(*a*) Vaporisation of a mole of ether (b. pt 35°C, L = 6500 cal/mole)
(*b*) Freezing of a mole of water at 0°C ($l = 80$ cal/gm)

[Ans. (*a*) 21.1 e.u. (*b*) -5.28 cal/°K]

14. 14. Estimate the change in entropy when

(*a*) 20 gm He is compressed from a pressure of 1 atm. to 10 atm. at 20°C
(*b*) 7 gm N_2 gas is heated from 300°K to 500°K at constant volume ($C_p = 7$ cal/mole).

[Ans. (*a*) -23 e.u. (*b*) 0.633 e.u.]

15. One mole of a diatomic gas ($C_v = 5$ cal) was initially at 25°C and 1 atm. The gas was transferred to the state of 100°C temperature and 10 atm pressure. Calculate the entropy-change.

[Ans. -3.02 e.u.]

CHAPTER 11

FREE ENERGY FUNCTIONS

Two other thermodynamic functions which are extensively used may now be introduced. These two functions are:

(1) *Helmholtz free energy or Work function, A*

(2) *Gibb's function or Gibb's free energy, G*

The latter is also called *thermodynamic potential.* These two are defined as

$$A = E-TS \qquad \ldots \text{(XI.1)}$$

$$G = H-TS \qquad \ldots \text{(XI.2)}$$

The quantity TS (product of temperature and entropy) has units of energy.

The functions E, H, T and S are state properties, hence A and G are both state functions. Their values depend only and only on the parameters of the system. The changes $\triangle A$ and $\triangle G$ are independent of the path of the transformation of the system.

Since $H = E+PV$, $G = H-TS = E+PV-TS = A+PV$

We shall use the term 'work function' for A and the term 'free energy' for G.

11.1. Work Function, A

$$A = E-TS$$

For an *isothermal reversible* change ($\triangle T = 0$),

$$\triangle A_T = \triangle E-T\triangle S = \triangle E-q$$

or

$$\triangle A_T = -w_{\max}$$

where $w_{\max}$ is the reversible, hence maximum, work involved.

$$-\triangle A_T = w_{\text{rev}} \qquad \ldots \text{(XI.3)}$$

It may then be said that the *work function*, A is such a thermodynamic property of the system that its decrease gives the maximum amount of work available during an isothermal transformation of the system. This work may be purely mechanical or otherwise or may be partly mechanical and partly external.

It should however be remembered that (*i*) if the same transformation be irreversible then the same drop in A would occur but it would exceed the output of work, *i.e.*, $-\triangle A > w$.

(*ii*) if the change be not isothermal, the change in work function A will not be equivalent to the maximum work.

$$dA = dE-TdS-SdT = dE-q-SdT$$

or

$$dA = -PdV-SdT \qquad \ldots \text{(XI.4)}$$

$$\therefore \quad \left(\frac{\partial A}{\partial V}\right)_T = -P \text{ and } \left(\frac{\partial A}{\partial T}\right)_V = -S \qquad \ldots \text{(XI.5)}$$

11.2. Free Energy, G

$$G = H - TS = E + PV - TS$$

So, $\triangle G = \triangle E + P\triangle V + V\triangle P - T\triangle S - S\triangle T$

For an isothermal reversible change of the system at constant pressure,

$$\therefore \quad \triangle G_{P,T} = \triangle E + P\triangle V - T\triangle S = \triangle E + P\triangle V - q$$

$$= P\triangle V - w_{\text{rev}}$$

or $\quad -\triangle G_{P,T} = w_{\text{rev}} - P\triangle V \qquad \ldots \text{(XI.6)}$

where $P\triangle V$ is the mechanical work involved in the system itself during the transformation for its expansion or contraction and w denotes the maximum total work output.

Hence $w - P\triangle V$ is the amount of work received for any external use, exclusive of the mechanical work in the change of the system itself.

Free energy (G) is thus a property of the system whose decrease is the measure of the external work available during the transformation of the system. It should be remembered that the relation (XI.6) holds true in isothermal reversible processes.

Again, in general, $dG = dE + PdV + VdP - TdS - SdT$

Since $dE + PdV = TdS$; $\quad dG = VdP - SdT \qquad \ldots \text{(XI.7)}$

Hence $\qquad \left(\frac{\partial G}{\partial T}\right)_P = -S \qquad \ldots \text{(XI.8)}$

$$\left(\frac{\partial G}{\partial P}\right)_T = V \qquad \ldots \text{(XI.9)}$$

Since chemical reactions are mostly carried out at constant P and T, the studies in chemical processes are more concerned with free energy changes ($\triangle G$).

11.3. Gibbs-Helmholtz Relation

In an isothermal change of a system,

$$G_1 = H_1 - TS_1 \qquad \text{and} \qquad G_2 = H_2 - TS_2$$

The suffix 1 for initial state and 2 for final state of the system,

Subtracting, $\qquad \triangle G = \triangle H - T\triangle S \qquad \ldots \text{(XI.10)}$

This is very important, for, from the values of $\triangle H$ and $\triangle S$ (measurable) the free energy change would be known.

Now from (XI.8), $\quad \triangle S = S_2 - S_1 = -\left[\left(\frac{\partial G_2}{\partial T}\right)_P - \left(\frac{\partial G_1}{\partial T}\right)_P\right]$

or $\qquad \triangle S = -\left[\frac{\partial(\triangle G)}{\partial T}\right] \qquad \ldots \text{(XI.11)}$

Substituting in eqn. (XI.10),

$$\triangle G = \triangle H + T\left[\frac{\partial(\triangle G)}{\partial T}\right]_P \qquad \ldots \text{(XI.12)}$$

The equations (XI.10) and (XI.12) are called 'Gibbs Helmholtz equations'.

For the work function, a similar treatment gives the relations

$$\triangle A = \triangle E + T\left[\frac{\partial(\triangle A)}{\partial T}\right]_V \quad \text{. . . (XI.13)}$$

11.4. Spontaneity of Chemical Process

The evaluation of free energy change permits the prediction of as to whether a chemical process would occur or not. For a given process, $\triangle E$ will be always the same. From the 1st Law, then

(*a*) for reversible occurrence, $q_{rev} = \triangle E + w_{rev}$

(*b*) for irreversible occurrence, $q_{irr} = \triangle E + w_{irr}$

But we know $w_{rev} > w_{irr}$, hence $q_{rev} > q_{irr}$.

Therefore for an infinitesimal change,

$$dq_{irr} - dq_{rev} < 0 \quad \text{. . . (A)}$$

By definition $dG = dE + PdV + VdP - TdS - SdT$

$$= q + VdP - TdS - SdT$$

Since chemical processes are carried out usually at a constant pressure and temperature,

$$\triangle G_{P,T} = q - TdS$$

Hence for a spontaneous irreversible chemical process.

$$dG_{P,T} = q_{irr} - TdS = q_{irr} - q_{rev}$$

Hence from (*A*), $dG_{P.T} < 0$

That is, for a chemical reaction to occur spontaneously $\triangle G$ must be *negative.*

To find out if a given reaction would occur at a given *T* and *P*, we have only to calculate $\triangle G$ of the system alone.

(*i*) The change will be spontaneous, if $\triangle G$ is *negative*

(*ii*) The system will remain in equilibrium, if $\triangle G = 0$

(*iii*) The process as desired will not occur, if $\triangle G$ is *positive.*

We may illustrate these with examples:

Example (1). For the process, $N_2O \rightarrow N_2 + \frac{1}{2}O_2$; $\triangle H = -20$ Kcal and $\triangle S = +18$ e.u., Will the reaction be spontaneous at 25°C?

$$\triangle G = \triangle H - T\triangle S = -20000 - 298 \times 18 = -25364 \text{ cal}$$

Since $\triangle G$ is negative, the dissociation will be spontaneous.

Example (2). Discuss the feasibility of the water gas reaction at 100°C and 1000°C. Given.

$$C + H_2O(g) \rightarrow CO(g) + H_2(g); \quad \triangle H = +31400; \quad \triangle S = 32 \text{ e.u.}$$

Now, $\triangle G_{100°C} = \triangle H - T\triangle S = 31400 - 373 \times 32 = +19464$ cal

$\triangle G_{1000°C} = \triangle H - T\triangle S = 31400 - 32 \times 1273 = -9336$ cal

At 100°C $\triangle G$ is positive, hence reaction shall not occur. At 1000°C, $\triangle G$ is negative, hence the reaction would easily take place.

11.5. The change of phase: Clapeyron-Clausius Equation

The thermodynamic relations are very useful in the study of changes of phase in a system, such as freezing, melting, vaporisation, etc. In phase-changes, a correlation exists between the pressure and the temperature at which the change takes place. This relation can be derived in different ways.

I. From Gibbs-Helmholtz Equation: Let G_1 and G_2 be the free energies of two phases (say solid and liquid, or liquid and vapour) *in equilibrium* at a given temperature T. Imagine a small virtual change of one phase into another (melting, freezing or vaporisation) under conditions of equilibrium. Let the drop in free energy of phase I be $-\triangle G_1$ and the increase in free energy of phase II be $+\triangle G_2$. Since the system is in equilibrium, net $\triangle G = 0$.

$$\therefore \qquad -\triangle G_1 + \triangle G_2 = 0\,; \qquad \text{or } \triangle G_1 = \triangle G_2$$

From eqn. (XI.7); $V_1 \triangle P - S_1 \triangle T = V_2 \triangle P - S_2 \triangle T$

$$\text{or} \qquad \frac{\triangle P}{\triangle T} = \frac{S_2 - S_1}{V_2 - V_1} = \frac{T\triangle S}{T(V_2 - V_1)} = \frac{L}{T(V_2 - V_1)}$$

$$\text{or} \qquad \frac{dP}{dT} = \frac{L}{T(V_2 - V_1)} \qquad \ldots \text{(XI.14)}$$

$T\triangle S = q$, the heat-change of the process. Hence $T\triangle S = L$, the latent heat of the phase-change.

This is known as the Clapeyron-Clausius Equation.

For freezing or melting of solid, L will be the latent heat of fusion ; for vaporisation L will be the latent heat of vaporisation.

II. From Carnot Cycle: Let 1 mole of liquid in a cylinder be reversibly vaporised under its saturation pressure P_1 at the temperature T. The volume V_1 of the liquid changes into the volume V_2 of the vapour. The change in volume $= (V_2 - V_1)$, as in Fig. XI. 1. The vaporisation would occur at constant saturation pressure P_1. The heat absorbed during the process is L, the latent-heat of vaporisation. The vapour is then adiabatically expanded to pressure P_2, when the temperature is lowered to T,′ so that $T - T' = \triangle T$. It is now reversibly condensed under pressure P_2 and temperature T'. The liquid is finally adiabatically compressed to its initial state of P_1 and T. The cycle is complete.

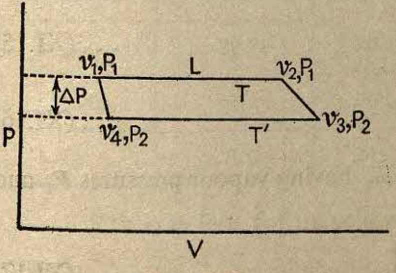


Fig. XI.1

The maximum work obtained would be the area of the parallelogram;

$$w = \Delta P\,(V_2 - V_1).$$

Applying the Second Law, $w = Q\frac{\Delta T}{T}$, we have

$$\Delta P(V_2 - V_1) = L\frac{\Delta T}{T}$$

or

$$\frac{dP}{dT} = \frac{L}{T(V_2 - V_1)} \qquad \text{... (XI. 14a)}$$

This Clapeyron-Clausius Equation is applicable to all phase-changes including sublimation, transition of solids, etc.

The sign of $\frac{dP}{dT}$ depends on the signs of L and ΔV. If L is positive and $V_2 > V_1$; dP/dT is positive and there will be rise in pressure with increase in temperature. In the vaporisation of liquids these conditions prevail, hence vapour pressure of liquids rise with increase in temperature. The same is true for sublimation.

In the melting of a solid, L is positive. If $V_l > V_s$, $\frac{dP}{dT}$ would be positive. Hence melting point would increase with increased pressure as in the case of a paraffin. If $V_s > V_l$; $\frac{dP}{dT}$ would be negative, the m. pt. will decrease with increase in pressure, as is found in the case of ice.

The Clapeyron Equation may be simplified in the case of vaporisation of a substance. In such a case

$$\frac{dP}{dT} = \frac{L_v}{T(V_g - V_l)}; \qquad (V_g = \text{Vol. of gas}, V_l = \text{Vol. of liquid}) .$$

Since $V_g \gg V_l$, so approximately,

$$\frac{dP}{dT} = \frac{L_v}{TV_g} = \frac{L_v}{RT^2/P} = \frac{L_v P}{RT^2} \quad \text{(for 1 mole)}$$

assuming the vapour to behave as an ideal gas. (L_v = molar latent heat of vaporisation).

Rewriting,

$$\frac{1}{P}\frac{dP}{dT} = \frac{L_v}{RT^2}, \qquad \text{... (XI.15)}$$

or

$$\frac{d\ln P}{dT} = \frac{L_v}{RT^2} \qquad \text{... (XI.16)}$$

Integrating between two temperatures T_1 and T_2 having vapour pressures P_1 and P_2, and assuming L_v to remain constant,

$$\ln\frac{P_1}{P_2} = -\frac{L_v}{R}\left[\frac{1}{T_1} - \frac{1}{T_2}\right] \qquad \text{... (XI.17)}$$

or

$$\log\frac{P_1}{P_2} = -\frac{L_v}{2.303R}\left[\frac{1}{T_1} - \frac{1}{T_2}\right] \qquad \text{... (XI.17a)}$$

This equation enables computation of vapour pressure of a liquid at a temperature if the same at another temperature be known.

Problem: Calculate the freezing point of water if the pressure be increased by 1 atm. ($l = 80$ cal/gm, specific volume of ice = 1.09 c.c.)

The latent-heat for freezing = -80 cal = $-80 \times 4.2 \times 10^7$ ergs.

The change in volume = $V_{ice} - V_{water} = 1.09 - 1.00 = 0.09$ c.c.

$$\frac{\triangle P}{\triangle T} = \frac{L}{T(V_{ice} - V_{liq})}$$

$$\therefore \quad \triangle T = \frac{\triangle P . T(V_{ice} - V_{liq})}{L} = \frac{13.6 \times 981 \times 76 \times 273 \times 0.09}{-80 \times 4.2 \times 10^7}$$

$$= -0.008°C$$

Problem: Under what pressure will water boil at 98°C ($l = 536$ cal/gm)?

$$\triangle P = \frac{L.P}{RT^2} \triangle T = \left[\frac{18 \times 536 \times 760}{2 \times 373^2} . (-2) \right] \text{mm} = -54 \text{ mm}$$

$\therefore$ Water will boil at 98°C under 706 mm pressure.

11.6. Trouton's Rule: The equation (XI.16) is

$$\frac{dlnP}{dT} = \frac{L_v}{RT^2} \qquad \text{or} \qquad \int dln\,P = \int \frac{L_v}{RT^2} dT$$

i.e.

$$ln\,P = -\frac{L_v}{RT} + Z_1 \text{ (constant)}$$

At the normal boiling pt. of the liquid $T = T_b$, and $P = 1$ atm and $ln\,P = 0$.

$$\therefore \quad \frac{L_v}{RT_b} = Z_1, \quad \text{or} \quad \frac{L_v}{T_b} = \text{constant} \qquad \text{. . . (XI.18)}$$

where Lv is the molar heat of vaporisation.

Trouton made this generalisation from exprimental observations and stated that *the ratio of the molar heat of vaporisation to the boiling temperature is a constant for simple or non-associated liquids and the constant is approximately* 21. (See Sec. 5.3).

Liquids	n-hexane	n-octane	benzene	toluene	O-xylene	CS_2
L/T_b	20.28	20.96	20.81	20.85	21.07	21.0
Liquids	HBr	NH_3	H_2O	H_2	N_2	O_2
L/T_b	21.0	24.2	28.7	15.6	17.3	18

The rule fails for associated liquids and for very low-boiling liquids.

11.7. The Standard Free Energy : Chemical Potential

The free energy is a state function. To assign numerical values to G, it is necessary to put a standard value for the free energy of the system at a specified state. The standard state is usually taken as at a temperature of 25°C and pressure 1 atm for a pure substance.

Now, at a constant temperature, from eqn.XI,

$$\left(\frac{dG}{\partial P}\right)_T = V, \quad \text{or} \quad \int_1^{\text{II}} dG = \int_{1\,\text{atm}}^{P} VdP$$

$$\text{or} \qquad G - G^\circ = \int_{1\,\text{atm}}^{P} VdP \qquad \text{. . . (XI.19)}$$

where G° is the free energy at 1 atm, temperature being constant. This relation applies to all systems.

If the system be one of n moles of an ideal gas at temperature T, then

$$G = G^\circ + \int_1^P \frac{nRT}{P} dP = G^\circ + nRT\, ln \frac{P\,\text{atm}}{1\,\text{atm}}$$

$$\text{or} \qquad G = G^\circ + nRT\, ln\, P \qquad \text{. . . (XI.20)}$$

$$\text{or, for 1mole} \qquad G/n = G^\circ/n + RT\, ln\, P$$

$$i.e., \qquad \bar{G} = \bar{G}^\circ + RT\, ln\, P \qquad \text{. . . (XI.21)}$$

$\bar{G}$, $\bar{G}^\circ$ are the corresponding free energies for 1 mole of the gas. The 'bar' overhead refers to one mole of the substance.

The free energy of 1 mole of a pure substance has been given the name **Chemical Potential** and is denoted by the symbol μ. Therefore, $\bar{G} = \mu$. We can then rewrite equation XI.21, as

$$\mu = \mu^\circ + RT\, ln\, P \qquad \text{. . . (XI.22)}$$

where μ° is the chemical potential of 1 mole under standard condition.

Mixtures: If a system contains ($n_1, n_2, n_3, \ldots$ moles) of several components having chemical potentials μ_1, μ_2, μ_3, etc. then the total free energy (G) of the system is given by

$$G = \mu_1 n_1 + \mu_2 n_2 + \mu_3 n_3 + \ldots \qquad \text{. . . (XI.23)}$$

If the amounts of components change by $dn_1, dn_2, dn_3 \ldots$ moles (T constant), then the change in free energy dG would be,

$$dG = \mu_1 dn_1 + \mu_2 dn_2 + \mu_3 dn_3 + \ldots \qquad \text{. . . (XI.24)}$$

11.8. Chemical Potentials and Concentration: Activity

The molar free energy or chemical potential (μ) is given (eqn.XI.21,22) for an ideal gas, as

$$\mu = \mu^\circ + RT\, ln\, P$$

In a mixture of ideal gases, the chemical potential for any component, say ith component, is expressed as

$$\mu_i = \mu_i^\circ + RT\, ln\, p_i \;;\; (p_i = \text{partial pressure}) \qquad \text{. . . (XI.25)}$$

Since the pressure is proportional to its mol-fraction x_i as also to its molar concentration C_i, μ can be expressed as

$$\left.\begin{aligned} \mu_i &= \mu_i^\circ + RT \ln x_i \\ \text{and} \qquad \mu_i &= \mu_i^\circ + RT \ln C_i \end{aligned}\right\} \qquad \ldots \text{(XI.26)}$$

μ°_i should be taken in respective concentration units.

When the system is a nonideal mixture or solution, corrections are required for the expressions given above. Retaining the form, the chemical potential in such cases is given by

$$\mu_i = \mu_i^\circ + RT \ln \gamma_i x_i \qquad \ldots \text{(XI.27)}$$

and

$$\mu_i = \mu_i^\circ + RT \ln f_i C_i \qquad \ldots \text{(XI.28)}$$

f_i, γ_i are called activity co-efficients of the *i*-th component. As the system tends to ideal behaviour, $\gamma_i \rightarrow 1$, $f_i \rightarrow 1$.

The quantity $\gamma_i x_i$ and $f_i C_i$ are called activity of the *i*th component and are denoted by 'a_i'. Hence

$$\mu_i = RT \ln a_i + \mu_i^\circ \qquad \ldots \text{(XI.29)}$$

If the mixture be an ideal one, a_i can be replaced by x_i or C_i as in eqn. (XI.26).

EXERCISES

1. Define free energy, G. Explain clearly its meaning and its distinction from work function. How does free energy change with variation of pressure?

2. Show that the maximum useful work is not necessarily equal to the heat of reaction.

3. Deduce Gibbs-Helmholtz equation and explain its significance.

4. Write notes on: (*a*) work function (*b*) Trouton's rule (*c*) Chemical potential (*d*) activity.

5. Discuss the criteria for predicting the feasibility of a chemical process.

6. Prove: (*i*) $$\left(\frac{\partial(\Delta G)}{\partial T}\right)_P = \frac{\Delta G - \Delta H}{T}$$

(*ii*) $$\mu_2 = \mu^\circ_2 + RT \ln a_2$$

7. Derive Clausius Clapeyron Equation. Explain why increase of pressure sometimes increases the melting point and sometimes decreases the melting point.

8. The standard free energy of SO_2 is −71.8 Kcal/mole. Calculate the molar free energy of SO_2 at 25°C and 10 atm. (C.U.)

9. At 25°C, the entropy-change of formation of $C_6H_{12}(l)$ is 49.3 Kcal.

$$6C + 6H_2 = C_6H_{12}(l); \qquad \Delta H = -37680 \text{ Cal}$$

Estimate the free energy of formation of $C_6H_{12}(l)$.

10. At what pressure will water boil at 101°C? Why does a housewife prefer a pressure-cooker for her cooking? [Ans. 786.36 mm]

11. The latent heat of vaporisation of water at 100°C is 540 cal/gm. At what temperature will water boil under 780 mm pressure? [Ans. 100.74°C]

12. The vapour pressure of toluene at 40.3°C and 18.4°C are 60 mm and 20 mm. Estimate the latent heat of vaporisation of toluene. [Ans. 9110 cal/mole]

13. If the talent heat of vaporisation of water at 100°C be 542 cal/gm, calculate the vapour pressure of water at 90°C. [Ans. 529 mm]

14. What is the latent heat of fusion of tin (m.p. 504°K) if its m.pt. is raised by 0.328°C when pressure is increased by 10 atm? The volume change is 0.03894 c.c./gm [Ans. 14.48 cal/gm]

15. The vapour pressures of BCl_3 at 10°C and 20°C are 562.9 and 807.5 mm. Find out its heat of vaporisation and its boiling point. [Ans. L_v = 5995 cal; 18.3°C]

16. At 100°C, dP/dT for water is 2.717 cm. The specific volumes of water vapour and liquid water are 1674 c.c. and 1.0 c.c. Calculate the molar heat of vaporisation. (Viswa Bharati) [Ans. 9720 cal/mole]

CHAPTER 12

THE CHEMICAL EQUILIBRIUM

12.1. Reversible Reactions: Equilibrium

It is common knowledge that many reactions do not go to completion even when favourable external conditions are maintained. The reactions proceed to some extent and then they come to a stop. The reaction between ethyl alcohol and acetic acid to form ester is a classic example.

$$CH_3COOH + C_2H_5OH \rightleftharpoons CH_3COOC_2H_5 + H_2O$$

In 1862, Berthelot and St. Gilles showed that if equimolar quantities of the acid and alcohol are taken, the reaction proceeds until about 67 percent of the reactants are transformed. The reaction then seems to stop with 33% of reactants unaltered. Alternatively. if a mixture of ester and water is taken, the reaction takes place in the opposite direction and stops when 33% of the ester is hydrolysed.

The reactions which are found to proceed simultaneously in both the directions are called **Reversible Reactions.** The reversibility is indicated by double arrows ($\rightleftharpoons$) in opposite directions.

To cite another instance, if equimolar amounts of hydrogen and iodine vapour be kept in a closed vessel at a constant temperature (360°C) and the contents are analysed at various time intervals, it is observed that the reaction stops when 80% of the gases are converted to hydrogen iodide. On the other hand, if hydrogen iodide be similarly treated the reaction comes to a stop when only 20% HI has decomposed. That is, the proportion of hydrogen, iodine and hydrogen iodide in the mixture will be the same in both the experiments. The composition will remain constant for unlimited time provided the temperature is constant. When such a stage is reached in the course of a reaction that no further action is apparent, the reaction is said to have attained **Equilibrium** at that temperature. It is obvious that (*i*) reaction can proceed either way and (*ii*) the composition of the system at equilibrium is fixed and (*iii*) the reaction cannot proceed to completion in either direction. These are the criteria of the eqm. state of a chemical process. The composition of the system at equilibrium would of course depend on the temperature.

The cessation of the chemical reaction at eqm. is however only apparent. In fact when equilibrium is attained, the reactions proceed in both the directions at equal rates. The amount of reactants disappearing per unit time is reproduced from the resultants at the same rate. The equilibrium is thus a dynamic one and not static.

Some common instances of reversible reactions:

Homogeneous: (*i*) $N_2 + 3H_2 \rightleftharpoons 2NH_3$

(*ii*) $2NO \rightleftharpoons N_2 + O_2$

(*iii*) $CO + H_2O \rightleftharpoons CO_2 + H_2$

(*iv*) $KI + I_2 \rightleftharpoons KI_3$

Hetrogeneous:

$$CaCO_3 \rightleftharpoons CaO + CO_2$$
$$3Fe + 4H_2O \rightleftharpoons Fe_3O_4 + 4H_2$$
$$C + H_2O \rightleftharpoons CO + H_2$$

In many cases, it seems that the reaction proceeds practically to completion in one direction, such as decomposition of potassium chlorate or the reaction between silver nitrate and sodium chloride solutions. These are often mentioned as *irreversible reactions.*

$2KClO_3 \rightarrow 2KCl + 3O_2$ $AgNO_3 + NaCl \rightarrow AgCl + NaNO_3$

But indeed all chemical reactions are reversible. The extent of the opposite reaction is so small as to be negligible and for that reason, it seems the reaction is unidirectional. Hence, for a reversible reaction to be recognised, the forward and the reverse reaction both occur to a noticeable extent.

12.2. The Law of Mass Action

A quantitative relation between the amounts of the reactants and the resultants at eqm. was developed from a basic principle, called the **Law of Mass Action,** first enunciated by two Norwegian chemists, Guldberg and Waage (1867).

The law states: *At a constant temperature, the rate of a chemical reaction is proportional to the 'active masses' of the reacting substances.*

The expression 'active mass' in the statement requires serious consideration. For ordinary systems as those of gases or dilute solutions, which do not deviate appreciably from ideal behaviour, active mass may be taken to mean molar concentration. For solids and pure liquids, the active masses or concentrations are taken as unity since the rate of reaction is independent of their amounts present.

The rate of reaction is the change in concentration per unit time; rate $= dc/dt$.

Consider a reversible reaction; $A + B \rightleftharpoons C + D$

$$(Conc.: \; C'_A \;\; C'_B \qquad C'_C \;\; C'_D)$$

Let C'-terms denote the concentrations of the components at a given instant during the progress of the reaction. According to the law, the rate of reaction (R_{AB}) between A and B at that moment will be

$$R_{AB} = k_1 C'_A . C'_B$$

where k_1, the constant of proportionality, depends upon reactants and temperature. The concentrations of the reactants (A and B) would diminish with the progress of reaction and hence its rate would diminish with time.

Similarly, the rate of the opposite reaction (R_{CD}) between C and D at that moment will be

$$R_{CD} = k_2 C'_C . C'_D$$

k_1, and k_2 are called *velocity constants* for the opposite reactions.

With the progress of reaction, the concentrations of C and D would increase and hence the rate R_{CD} would increase with time. A time will come when the rates of reaction in the two opposite directions would be equal, *i.e.*, $R_{AB} = R_{CD}$. The system would then attain equilibrium and there would be no further change in the masses of the components of the system. At equilibrium, let the concentrations be expressed by C-terms (instead of C'). Then,

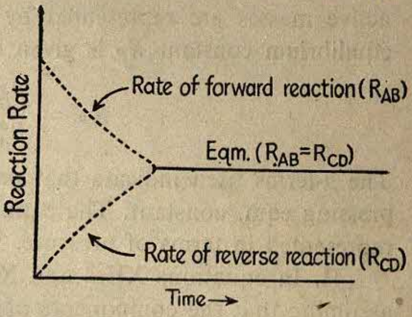


Fig. XII.1. Attainment of epm.

$$R_{AB} = R_{CD}$$

or $$k_1C_AC_B = k_2C_CC_D$$

or $$\frac{C_CC_D}{C_AC_B} = \frac{k_1}{k_2} = K_C \text{ (constant)} \qquad \ldots \text{(XII.1)}$$

K_C is called the *equilibrium constant* of the reaction. C_C, C_D, C_A, C_B etc. are the concentrations of the species at eqm. If the eqm. lies well over to the side of the resultants K_C will be large, whereas if it lies well over to the side of the reactants K_C will be small.

The initial concentrations may be varied but at a given temperature, equation (XII.1) will be valid for any given reversible reaction. Furthermore the state of equilibrium can be reached starting either with A and B or with C and D.

In the case cited above one molecule only of each of the reactants was involved. Let us take an example now with more than one molecule of a species entering into the reaction; say,

$$2A + 3B \rightleftharpoons C + 2D$$

the rates are given by, $$R_{AB} \rightleftharpoons k_1C_A^2C_B^3$$

and $$R_{CD} \rightleftharpoons k_2C_CC_D^2$$

At equilibrium, $$k_1C_A^2C_B^3 = k_2C_CC_D^2$$

or $$K_C = \frac{k_1}{k_2} = \frac{C_CC_D^2}{C_A^2C_B^3}$$

The eqm. constant (K_C) is the product of the concentrations of the resultants (on the right side) divided by the product of the concentrations of the reactants (on the left side). The concentrations of the different species have to be raised to powers which are coefficients of the respective species in the stoichiometric equation.

In general, for a reversible reaction of the type,

$$a\,\mathrm{A} + b\,\mathrm{B} + \ldots \rightleftharpoons g\,\mathrm{G} + h\,\mathrm{H} + \ldots$$

the eqm. constant,

$$K_c = \frac{C_G^g \times C_H^h \times \ldots}{C_A^a \times C_B^b \times \ldots} \qquad \ldots \text{(XII.2)}$$

Two relevant matters may be mentioned here.

I. If the reversible reaction $aA + bB \rightleftharpoons gG + hH$, be a gaseous one, the active masses are represented by partial pressures of the different species. Its equilibrium constant K_P is given by,

$$K_P = \frac{p_G^g \times p_H^h \times \ldots}{p_A^a \times p_B^b \times \ldots} \qquad \ldots (XII.3)$$

The p-terms used indicate that partial pressures of gases have been used in expressing eqm. constant. The eqm. constant K_P (with suffix P) means that it is represented in terms of pressure.

II. In equations XII.2 and XII.3, the eqm. constants have been derived by assuming that the components of the system more or less behave ideally. But at high concentrations or pressures, the effective concentrations would differ from molar concentrations. It would be more accurate if *activities* of the species are used in place of molar concentrations or partial pressures. The 'activity' is indeed concentration corrected for non-ideality.

The activity, $a = fc$, where f is the activity co-efficient. In very dilute solutions or low pressures, $f = 1$, hence activity is the same as the concentration (see sec. 11.7), Hence, the eqm. constant K_a in terms of activities for the reaction,

$$aA + bB \rightleftharpoons gG + hH$$

$$K_a = \frac{a_G^g \times a_H^h}{a_A^a \times a_B^b}$$

Since $a = fc$, we can write,

$$K_a = \frac{C_G^g \times C_H^h}{C_A^a \times C_B^b} \times \frac{f_G^g \times f_H^h}{f_A^a \times f_B^b} = K_c \times \phi(f)$$

$\phi(f)$ is a function of the activity coefficients.

For ideal systems, $K_a = K_c$, for f-terms would be unity *i.e.* $\phi(f) = 1$.

12.3. Relation between K_p & K_c

For the reversible reaction, $aA + bB \rightleftharpoons gG + hH$,

$$K_P = \frac{p_G^g \times p_H^h}{p_A^a \times p_B^b}$$

But assuming ideality, the partial pressures are

$$p_A = C_ART, \quad p_B = C_BRT, \quad p_G = C_GRT, \quad p_H = C_HRT, \text{ etc.}$$

$$\text{Hence } K_p = \frac{(C_GRT)^g \times (C_HRT)^h}{(C_ART)^a \times (C_BRT)^b} = \frac{C_G^g \times C_H^h}{C_A^a \times C_B^b} \times (RT)^{(g+h)-(a+b)}$$

or

$$K_p = K_c \times RT^{\Delta\nu} \qquad \ldots (XII.4)$$

where $\Delta\nu = (g + h) - (a + b)$ = the *number of resultant molecules—the number of reactant molecules.*

when the numbers of reactant and resultant molecules are equal as in

$$2NO = N_2 + O_2,\ \triangle\nu = 0.\ \text{So, } K_p = K_c,$$

Example; At 400°, for the reaction, $N_2 + 3H_2 \rightleftharpoons 2NH_3$, $K_c = 0.50$. Calculate K_p.

$$K_p = K_c.(RT)^{\triangle\nu} = 0.50\,(0.082 \times 673)^{-2} = 1.6 \times 10^{-4}$$

for, $\triangle\nu = 2-(3+1) = -2$

The magnitudes of the eqm. constants depend upon the way the stoichiometric equation is written. Thus for the synthesis of ammonia,

$$N_2 + 3H_2 \rightleftharpoons 2NH_3;\ K_c = \frac{C^2_{NH_3}}{C_{N_2} \times C^3_{H_2}} = 0.50 \qquad \ldots (A)$$

or

$$\tfrac{1}{2}N_2 + \tfrac{3}{2}H_2 \rightleftharpoons NH_3\ ;\ K_c = \frac{C_{NH_3}}{C^{1/2}_{N_2} \times C^{3/2}_{H_2}} = 0.707 \qquad \ldots (B)$$

If the equation for the reaction is reversed, the new K_c will be the reciprocal of the former one.

$$2NH_3 \rightleftharpoons N_2 + 3H_2,\ \ K_c = \frac{C_{N_2} \times C^3_{H_2}}{C^2_{NH_3}} = 2.00$$

The units for K_c or K_p will be determined by the net powers of the concentrations or partial pressures involved in their expressions. In the equation (A) above, the unit is moles^{-2} litre^2. and in the eqn (B), the unit would be mole^{-1} litre^1.

12.4. The dynamic nature of the equilibrium

That the equilibrium state is not static but the process continue in opposite directions at equal rates has now been experimentally demonstrated in many cases. To cite an instance, the reaction involving oxidation of arsenious acid to arsenic acid by iodine attains equilibrium easily. The proportion of arsenious and arsenic acid is determined at eqm.

$$H_3AsO_3 + KI_3 + H_2O \rightleftharpoons H_3ASO_4 + KI + H_2O$$

The experiment on being repeated under same conditions with arsenious acid part of which is radioactive, it is observed that the net equilibrium remains the same. But even after attainment of equilibrium the radioactivity of the arsenic acid changes with time. This shows that the chemical reactions are continuing even after the equilibrium is reached.

It may be mentioned again that the eqm is reached from either direction. The presence of a catalyst influences the rate but not the eqm state.

12.5. Equilibrium Constant from Thermodynamic Considerations

Suppose the reaction

$$aA + bB \rightleftharpoons gG + hH$$

has attained equilibrium at a constant temperature T. Imagine a small virtual change in the system under conditions of equilibrium such that $\triangle x \times a$ moles of A diminishes. In consequence, B will diminish by $\triangle x \times b$ moles, while G and H would increase by amounts $\triangle x \times g$ and $\triangle x \times h$ moles.

If μ_A, μ_B, μ_G, μ_H denote their chemical potentials, then the net free-energy change would be

$$\triangle G = \triangle xg.\mu_G + \triangle xh.\mu_H - \triangle xa.\mu_A - \triangle xb.\mu_B = 0,$$

for at equilibrium $\triangle G = 0$. Hence

$$g\mu_G \times h\mu_H - a\mu_A - b\mu_B = 0$$

or
$$g\mu_G + h\mu_H = a\mu_A + b\mu_B \qquad \text{...(XII.5)}$$

That is, at equlibrium, the net free energy of the reactants is equal to the net free energy of the resultants.

Now, the molar free energy or chemical potential of a substance is given by

$$\mu = \mu^\circ + RTlna$$

where 'a' is the activity of the substance (Sec 11-7). μ° is a constant and denotes the standard free energy per mole. Substituting in eqn. (XII.5),

$$g(\mu^\circ_G + RTlna_G) + h(\mu^\circ_H + RTlna_H) = a(\mu^\circ_A + RTlna_A) + b(\mu^\circ_B + RTlna_B)$$

or
$$RTlna^g_G + RTlna^h_H - RTlna^a_A - RTlna^b_B = a\mu^\circ_A + b\mu^\circ - g\mu^\circ_G - h\mu^\circ_H = Z$$

(say).

or
$$ln\frac{a^g_G \times a^h_H}{a^a_A \times a^b_B} = \frac{Z}{RT} \text{ (constant)}$$

$$\therefore \qquad \frac{a^g_G \times a^h_H}{a^a_A \times a^b_B} = K_a \qquad \text{(XII.6)}$$

where K_a is the thermodynamic equilibrium constant.

In ideal systems, the activities may be replaced by molar concentrations or by partial pressures (for gaseous systems). So

$$\frac{C^g_G \times C^h_H}{C^a_A \times C^b_B} = K_c \quad \text{and} \quad \frac{p^g_G \times p^h_H}{p^a_A \times p^b_B} = K_P$$

These are the same as the empirically derived relations (eqns. XII.2 and 3). The law of mass action is thus established.

12.6. Experimental Method for determining Eqm. Constants

The methods employed to determine eqm constants are different for different equilibria. Often chemical analysis is employed. A classic example is the study of $2HI \rightleftharpoons H_2 + I_2$ by Bodenstein. Small glass bulbs of known volume were filled with HI gas at different pressures and sealed off. The bulbs were then kept in constant high temp. baths for a long time till eqm. is reached. The bulbs were then taken out and quickly cooled as to freeze the eqm. inside. The bulbs were then opened under caustic alkali solution which absorbs both HI and I_2. The hydrogen is collected in an eudiometer tube and the volume measured. The amount of hydrogen gives the extent of dissociation (α) from which K_p is known. In another set of experiments, known amounts of H_2 and I_2 are taken. The unreacted H_2 is estimated as before when eqm is reached. The value of K_p conforms to the previous result.

In hydrolysis of esters, *e.g.* $CH_3COOEt + H_2O \rightleftharpoons CH_3COOH + EtOH$, an aliquot part of the eqm mixture is taken out and immediately added to a large volume of ice-water. This freezes the equilibrium. The dilute cold solution is then titrated against a standard alkali solution from which the amount of acid formed at eqm is known. The eqm. constant can then be easily calculated.

Physical methods are also taken advantage of. For studying eqm. in mutarotation of glucose, polarimetric measurement reveals how much change has taken place. In ionic equilibria for the dissociation of organic acids, the conductance measurement of solutions is used to ascertain the dissociation constant.

Sometimes a system appears to have attained eqm. But if it be disturbed, say by adding a catalyst, or mechanically by shaking or by passing a momentary spark, it changes into a new state. The original apparent equilibrium is said to be a **metastable equilibrium.**

12.7. Equilibrium Constants of Some Typical Reactions

GASEOUS SYSTEMS

In the study of equilibria, gas reactions are broadly classified into two groups: (*i*) *First type gas reactions* in which total number of reactant molecules and of resultant molecules are the same, *i.e.*, $\triangle \nu = 0$, *e.g.*, $2HI \rightleftharpoons H_2 + I_2$ (*ii*) *Second type gas reactions* in which the number of molecules of reactants differ from that of the resultants, *i.e.*, $\triangle \nu \neq 0$, *e.g.*, $PCl_5 \rightleftharpoons PCl_3 + Cl_2$.

First Type Gas Reactions

(*i*) *Hydrogen-Iodine reaction*: $2HI \rightleftharpoons H_2 + I_2$

The method for determination of the equilibrium constant of this reaction by filling up small bulbs of known volumes with the reactant at different pressures and at constant temperature has been discussed in Sec. 12.6. When equilibrium is attained, the volume of hydrogen produced is measured in an eudiometer after removal of I_2 and HI with potash solution. This enables the computation of K_c as shown below.

Consider the following equilibrium in a vessel of volume V:

	$2HI \rightleftharpoons$	H_2	$+ I_2$	
Initial amounts:	a	0	0	moles
At equilibrium:	$a-x$	$\frac{x}{2}$	$\frac{x}{2}$	moles
Conc. at equilibrium:	$\frac{a-x}{V}$	$\frac{x}{2V}$	$\frac{x}{2V}$	moles/litre

Hence: $$K_c = \frac{C_{H_2} \times C_{I_2}}{C^2_{HI}} = \frac{\frac{x}{2V} \times \frac{x}{2V}}{\left(\frac{a-x}{V}\right)^2} = \frac{x^2}{4(a-x)^2}$$

This shows x is independent of volume, and hence of pressure as well. For,

$$K_p = K_c(RT)^{\triangle\nu} = K_c, \quad \text{since, } \triangle\nu = 0$$

(*ii*) *Water-gas reaction*: $H_2 + CO_2 \rightleftharpoons CO + H_2O$

This is also a 1st type gas reaction. Starting with equimolecular mixture of the reactants, we have, when x is the extent of H_2 used up at eqm,

	H_2	CO_2	H_2O	CO		Total
At eqm (moles)	$1-x$	$1-x$	x	x	=	2
Partial pressures	$\frac{1-x}{2}P$	$\frac{1-x}{2}P$	$\frac{x}{2}P$	$\frac{x}{2}P$	=	P

$$\therefore \quad K_p = \frac{P_{H_2O} \times P_{CO}}{P_{H_2} \times P_{CO_2}} = \frac{[(x/2)P]^2}{\left[\frac{(1-x)}{2}P\right]^2} = \frac{x^2}{(1-x)^2}$$

hence x is independent of pressure.

At 1260°K and 1 atm, the eqm. composition of this reaction is $CO_2 = 21.4$, $H_2 = 22.9$, and $CO = 27.8$ moles percent.

$$\text{So,} \qquad K_p = \frac{(27.8)^2}{21.4 \times 22.9} = 1.58$$

(*iii*) *The synthesis of Nitric acid*: It involves the reaction,

$$N_2 + O_2 \rightleftharpoons 2NO$$

It is an endothermic reaction and has to be carried out at very high temperature. If x be the amount of nitrogen transformed at eqm, then

	N_2	O_2	NO	Total
moles initially	a	b	0	$a+b$
moles at eqm.	$a-x$	$b-x$	$2x$	$a+b$
Partial pressures	$\frac{a-x}{a+b}P$	$\frac{b-x}{a+b}P$	$\frac{2x}{a+b}P$	P

$$\text{So,} \qquad K_p = \frac{P_{NO}^2}{P_{N_2} \times P_{O_2}} = \frac{\left(\frac{2x}{a+b}P\right)^2}{\left(\frac{a-x}{a+b}P\right)\left(\frac{b-x}{a+b}P\right)} = \frac{4x^2}{(a-x)(b-x)}$$

Hence, pressure has no influence on the production of nitric oxide. This oxide is then converted into nitric acid by further oxidation and dissolution in water.

Second Type Gas Reactions

(*i*) *Dissociation of Phosphorus pentachloride*: $PCl_5 \rightleftharpoons PCl_3 + Cl_2$

Let us start with one mole of PCl_5 and suppose the degree of dissociation is α

at equilibrium. Then the relative amounts of the components and their pressures would be:

	PCl_5	PCl_3	Cl_2	Total
Moles at eqm	$1-\alpha$	α	α	$= 1+\alpha$
Partial pressures	$\frac{1-\alpha}{1+\alpha}P$	$\frac{\alpha}{1+\alpha}P$	$\frac{\alpha}{1+\alpha}P$	$= P$
Concentrations	$\frac{1-\alpha}{V}$	$\frac{\alpha}{V}$	$\frac{\alpha}{V}$	$= \frac{1+\alpha}{V}$

V, the volume of the system.

Hence,
$$K_p = \frac{P_{PCl_3} \times P_{Cl_2}}{P_{PC_5}} = \frac{\left(\frac{\alpha}{1+\alpha}P\right)\left(\frac{\alpha}{1+\alpha}P\right)}{\frac{1-\alpha}{1+\alpha}P} = \frac{\alpha^2}{1-\alpha^2}P$$

and
$$K_c = \frac{C_{PCl_3} \times C_{Cl_2}}{C_{PCl_5}} = \frac{\frac{\alpha}{V}\cdot\frac{\alpha}{V}}{\frac{1-\alpha}{V}} = \frac{\alpha^2}{(1-\alpha)V}$$

Since the numbers of molecules of reactants and resultants are unequal, $K_p \neq K_c$. At any given temperature K_p remains constant, hence with increase of pressure P, α will diminish. That is, the extent of dissociation will decrease with pressure increase.

(*ii*) *Synthesis of ammonia*: $N_2 + 3H_2 \rightleftharpoons 2NH_3$

This is a reaction in which the number of molecules of resultants is less than that of the reactants. Suppose we start with a mixture of N_2 and H_2 in 1 : 3 ratio in moles and let the extent of chemical transformation at equilibrium be x per mole of nitrogen. Then

	N_2	H_2	NH_3	Total
Initial moles	1	3	0	$= 4$
Moles at equilibrium	$1-x$	$3-3x$	$2x$	$= 4-2x$
Partial pressures	$\frac{1-x}{4-2x}P$	$\frac{3-3x}{4-2x}P$	$\frac{2x}{4-2x}P$	$= P$

So,
$$K_p = \frac{P^2_{NH_3}}{P_{N_2} \cdot P^3_{H_2}} = \frac{\left[\frac{2x}{4-2x}P\right]^2}{\left[\frac{1-x}{4-2x}P\right]\left[\frac{3-3x}{4-2x}P\right]^3} = \frac{4x^2(4-2x)^2}{27(1-x)^4P^2}$$

If x is small,
$$K_p \approx \frac{64}{27} \cdot \frac{x^2}{P^2}$$

It shows K_p, which is constant at any given temperature, is determined by the ratio x/P. Further, with increase of P, x must also increase proportionately,

for
$$P^2 = \frac{64}{27K_p}x^2, \quad \textit{i.e.}, \; P = k'x$$

This means that with higher pressures, the yield of ammonia would be larger. This is a valuable information to the manufacturer of ammonia. We can also calculate K_c from this, by equation (XII.4),

$$K_c = K_p(RT)^{-\Delta\nu} = \frac{64x^2}{27}\cdot\frac{1}{P^2}\cdot(RT)^{-(2-4)} = \frac{64x^2}{27}\,(RT/P)^2$$

Since volume $V = (4-2x)\dfrac{RT}{P} \approx 4\,\dfrac{RT}{P}$, we have, $K_c = \dfrac{64x^2}{27}\left(\dfrac{V}{4}\right)^2 = \dfrac{4x^2V^2}{27}$.

(*iii*) The production of sulphuric acid involves the reaction:

$$2SO_2 + O_2 \rightleftharpoons 2SO_3$$

If x be the quantity of oxygen used up at eqm, then

	SO_2	O_2	SO_3	Total
moles initially	a	b	0	$a+b$
moles at eqm	$a-2x$	$b-x$	$2x$	$a+b-x$
Partial pressures	$\dfrac{(a-2x)P}{a+b-x}$	$\dfrac{(b-x)P}{a+b-x}$	$\dfrac{2xP}{a+b-x}$	P

$$\text{So,}\quad K_p = \frac{P^2_{SO_3}}{P^2_{SO_2}\times P_{O_2}} = \frac{\left[\dfrac{(2x)P}{a+b-x}\right]^2}{\left[\dfrac{(a-2x)P}{a+b-x}\right]^2\times\dfrac{(b-x)P}{(a+b-x)}} = \frac{4x^2(a+b-x)}{(a-2x)^2(b-x)P}$$

It shows that a greater yield of SO_3 is expected with increase of pressure. But even at ordinary pressure, the eqm is shifted much to the right, hence use of higher pressure is unnecessary. It will be seen later that higher temperature is also not required for the reaction is exothermic.

LIQUID SYSTEMS

The equilibrium in all systems — homogeneous and heterogeneous — is always governed by the law of mass action. The reactions in solutions or reactions between liquids are also studied in the same way as in the case of gases. The esterification of acids is a classical example of eqm. study in liquid systems.

(*i*) *Esterification of acetic acid*:

$$C_2H_5OH + CH_3COOH \rightleftharpoons CH_3COOC_2H_5 + H_2O$$

	C_2H_5OH	CH_3COOH	$CH_3COOC_2H_5$	H_2O	
At eqm.:	$a-x$	$b-x$	x	x	moles

Let the total volume of the liquid system be V and let the initial amounts of alcohol and acid be a and b gm-moles and at equilibrium the amount of acid esterified be x. Then at equilibrium, the concentrations are:

$$C_{\text{alc}} = \frac{a-x}{V},\quad C_{\text{acid}} = \frac{b-x}{V},\quad C_{\text{ester}} = \frac{x}{V},\quad C_{H_2O} = \frac{x}{V}$$

$$\text{So,}\qquad K_c = \frac{C_{\text{ester}}\times C_{H_2O}}{C_{\text{alc}}\times C_{\text{acid}}} = \frac{x^2}{(a-x)(b-x)}$$

The equilibrium constant is therefore independent of the volume of the system. If we start with 1 mole of each, then

$$K_c = \frac{x^2}{(1-x)^2}, \quad \text{or} \quad x = \frac{2K_c \pm \sqrt{4K_c^2-4(K_c-1)K_c}}{2(K_c-1)}$$

Experimentally, at room temperature, $K_c = 4.0$. So, $x = 0.66$. It is obvious that with a given amount of acid and alcohol, we can calculate the expected yield of the ester at equilibrium.

(*ii*) Another equilibrium studied carefully in a liquid system is esterfication with amylene (C_5H_{10});

$$CCl_3COOH + C_5H_{10} \rightleftharpoons CCl_3COOC_5H_{11}$$

$$\text{Conc.:} \quad (a-x)/V \quad (b-x)/V \quad x/V$$

If initial amounts of the acid and hydrocarbon be *a* and *b* moles in volume *V* and *x* moles be esterified at eqm, then

$$K_c = \frac{\frac{}{V}}{\frac{(a-x)}{V}\frac{(b-x)}{V}} = \frac{xV}{(a-x)(b-x)}$$

HETEROGENEOUS SYSTEMS

(*i*) *Dissociation of calcium carbonate.* This is a heterogeneous chemical reaction, as one of the products (CO_2) is in the gas-phase while others are solids.

$$CaCO_3 \rightleftharpoons CaO + CO_2$$

If, at a constant temperature, calcium carbonate is kept in a closed vessel, then the reaction proceeds with gradual increase in pressure of CO_2 until a constant pressure is obtained which is called the dissociation pressure of calcium carbonate.

It is the generally accepted convention that the activities of solids should be regarded as unity. In the case of liquids, the standard state is the pure state (under 1 atm), when activity is unity. But if it be present in liquid solution, as a first approximation, activity may be taken as equal to its mol-fraction.

Now, for dissociation of calcium carbonate, $a_{CaCO_3} = 1, a_{CaO} = 1$

$$\therefore \quad K_a = \frac{a_{CaO} \times a_{CO_2}}{a_{CaCO_3}} = a_{CO_2} \approx P_{CO_2}$$

assuming that the gas behaves ideally. Hence at any given temperature, the dissociation pressure of calcium carbonate would be a constant. If CO_2 is removed from the system continuously, more and more $CaCO_3$ would decompose to keep the constancy of P_{CO_2}. In other words, to obtain lime, CO_2-gas should continuously escape from the kiln.

(*ii*) *Hydrogen from steam by reduction with coke*

The reaction; $\quad C + H_2O \rightleftharpoons CO + H_2$

The eqm. constant,

$$K_a = \frac{a_{CO} \times a_{H_2}}{a_C \times a_{H_2O}} \approx \frac{P_{CO} \times P_{H_2}}{P_{H_2O}}; \quad (a_C = 1)$$

or $$K_a = \frac{P_{H_2}^2}{P_{H_2O}}, \quad \text{since } P_{CO} = P_{H_2}$$

That is, the ratio P_H^2/P_{H_2O} is constant. Obviously, to obtain a greater yield of hydrogen, the steam-pressure must be increased.

It would be interesting to know how the equilibrium state is altered in a gaseous system when

(*i*) a product of the reaction is added to the system at eqm.

(*ii*) a non-reacting gas is added to the system at eqm.

12.8. Effect of Addition of a Product on Equilibrium

If a product of the reaction is added to the system at eqm., its partial pressure immediately increases. To keep the value of K_p constant, the partial pressures of the other products would diminish. This results in the union of the products to reform the original reactant (*s*). In other words, the addition of a product will help the backward reaction.

Consider a reaction,

$$\begin{array}{lcccl} & X & \rightleftharpoons Y & + Z & ; \text{ so that } K_p = \dfrac{P_y . P_z}{P_x} \\ \textit{moles:} & b-a & c+a & a & \end{array}$$

If an excess amount of Y be added to the system at eqm., then P_z should decrease and P_x would increase, in order to maintain the constancy of K_p, *i.e., dissociation will be suppressed.*

Let '*b*' gm-moles of X be heated to a constant temperature in a vessel at constant pressure containing '*c*' gm-moles of Y. Suppose '*a*' gm-moles of X dissociate at eqm. Then the amounts of X, Y and Z would be $(b-a)$, $(c+a)$ and a gm-moles respectively. Total no. of gm. moles will be $\Sigma n = (b+c+a)$.

$$K_p = \frac{P_y \times P_z}{P_x} = \frac{\frac{n_y}{\Sigma n}P \times \frac{n_z}{\Sigma n}P}{\frac{n_x}{\Sigma n}P} = \frac{n_y . n_z}{n_x} . \frac{P}{\Sigma n} = \frac{(c+a)a}{(b-a)(b+c+a)}P$$

The value of '*a*' can be estimated from known values of K_p, b and c.

The same effect will be noticed in the case of solutions.

Since $K_c = \frac{C_y . C_z}{C_x}$, if the concentration of C_y be raised by adding some amount of Y, then C_z must diminish through backward reaction. In other words, the forward reaction would be suppressed.

12.8a. Effect of adding inactive gases to a system on equilibrium

$$\begin{array}{lcccc} \text{Consider the reaction:} & aA + bB & \rightleftharpoons gG & + hH \\ \text{moles at eqm:} & n_A \quad n_B & n_G & n_H \end{array}$$

Let n_0 gm-moles of a non-reacting gas be introduced into the system at eqm. The total quantity of gas in the system

$$= n_A + n_B + n_G + n_H + n_0 = \Sigma n \text{ (say)}$$

The partial pressures of the components would be

$$P_A = \frac{n_A}{\Sigma n}P,\quad P_B = \frac{n_B}{\Sigma n}P,\quad P_G = \frac{n_G}{\Sigma n}P,\quad P_H = \frac{n_H}{\Sigma n}P$$

$$\text{So,}\quad K_p = \frac{\left(\frac{n_G}{\Sigma n}P\right)\left(\frac{n_H}{\Sigma n}P\right)^h}{\left(\frac{n_A}{\Sigma n}P\right)^a\left(\frac{n_B}{\Sigma n}P\right)^b} = \frac{n_G{}^g \times n_H{}^h}{n_A{}^a \times n_B{}^b} \times \left(\frac{P}{\Sigma n}\right)^{\Delta\nu} \qquad \ldots (A)$$

where P = total pressure; $\Delta\nu = (g+h)-(a+b)$.

The addition of the inactive gas would always increase Σn. The effect of this addition may be considered separately in different cases.

I. *For first-type gas reactions*: The value of $\Delta\nu = 0$; hence $(P/\Delta n)^{\Delta\nu} = 1$. Hence in such a reaction, the first term of equation A above shall remain unaltered to maintain the constancy of K_p. The equilibrium state of 1st type gas reaction remains undisturbed on addition of a non-reacting gas.

II. *For Second-type gas reactions*: (*a*) If $\Delta\nu$ is positive, as the dissociation of PCl_5, $(P/\Sigma n)^{\Delta\nu}$ diminishes with increase in Σn; hence the first term of equation A will increase in magnitude to keep K_p constant.

This is possible by increasing the concentrations of resultants in the numerator and decreasing the concentrations in the denominator. In other words, there would be more of the reaction. At constant pressure, the presence of nitrogen would increase the dissociation of phosphorus pentachloride.

(*b*) For a reaction in which $\Delta\nu$ is negative, $(P/\Sigma n)^{\Delta\nu}$ increases with increase in Σn; hence the first factor must diminish to keep K_p constant. In other words, the concentrations of the resultants in the numerator must decrease. That is, the reaction will be depressed. So, at constant pressure the presence of argon would reduce the formation of ammonia from nitrogen and hydrogen.

III. When the inert gas is added at *constant volume*:

If the inert gas is added at constant volume, the total pressure P will increase proportionately with Σn; hence $(P/\Sigma n)$ will remain constant. Therefore, the first factor in equation will remain unchanged to keep K_p constant. That is, the equilibrium will not be disturbed.

12.9. Some numerical examples

Problem 1. At 25°C, 1 mole of acetic acid and 1 mole of ethanol are mixed. At eqm. 0.667 moles of acid have reacted. Calculate K_c. How much ester would be obtained if 2 moles of acid were taken with 1 mole ethanol under the same conditions?

$$K_c = \frac{C_{\text{ester}} \times C_{H_2O}}{C_{\text{acid}} \times C_{\text{alcohol}}} = \frac{(0.667/V)(0.667/V)}{(0.333/V)(0.333/V)} = 4.00$$

In the other experiment, let x moles of acid be transformed, then

$$\begin{array}{lcccc} & CH_3COOH & + \; EtOH & \rightleftharpoons \; CH_3COOEt & + \; H_2O \\ \text{Conc:} & (2-x)/V & (1-x)/V & x/V & x/V \end{array}$$

$$\therefore \qquad K_c = 4 = \frac{x^2}{(2-x)(1-x)} = \frac{x^2}{(2-3x+x^2)}$$

whence $x = 3.15$ or 0.85.

Since the first solution is absurd, amount of ester at eqm. is 0.85 moles.

Problem 2. Calculate the pressure required to obtain a 50% dissociation of PCl_5 at 250°C. The eqm. constant for the reaction, $PCl_5 \rightleftharpoons PCl_3 + Cl_2$; $K_p \rightleftharpoons 1.8$.

If 1 mole PCl_5 be present initially, then at eqm.,

$PCl_5 = 0.5$ moles and $PCl_3 = Cl_2 = 0.5$ moles. Total $= 1.5$ moles. The partial pressures of the different components would be the same,

$$p_{PCl_5} = p_{PCl_3} = p_{Cl_2} = (0.5/1.5)P = \tfrac{1}{3}P,$$

where P = total pressure in atmospheres.

$$\therefore \qquad K_p = \frac{p_{PCl_3} \times p_{Cl_2}}{p_{PCl_5}} = \frac{(\frac{1}{3}P)^2}{\frac{1}{3}P} = \tfrac{1}{3}P.$$

$$\therefore \qquad \tfrac{1}{3}P = 1.8, \text{ or } P = 5.4 \text{ atmospheres}$$

This shows that for a reaction of the type $AB \rightleftharpoons A + B$, the total pressure needed for 50% dissociation is numerically three times K_p.

Problem 3. At 25°C and 1 atm, Nitrogen tetroxide is dissociated to an extent of 18.46%. Calculate K_p. What will be the extent of dissociation at the same temperature if the pressure be 0.5 atm.?

$$\begin{array}{lccl} & N_2O_4 \rightleftharpoons & 2NO_2 & \text{Total} \\ & 1-\alpha & 2\alpha \;; & 1+\alpha \;; \quad \alpha = \text{degree of dissociation} \\ \text{Partial pressures:} & \dfrac{(1-\alpha)P}{1+\alpha} & \dfrac{2\alpha P}{1+\alpha} & P \end{array}$$

$$\therefore \qquad K_p = \frac{P^2_{NO_2}}{P_{N_2O_4}} = \frac{[2\alpha P/(1+\alpha)]^2}{(1-\alpha)P/(1+\alpha)} = \frac{4\alpha^2 P}{1-\alpha^2}$$

$$= \frac{4 \times (0.1846)^2}{1-(0.1846)^2} \times 1 = 0.141$$

Again at 0.5 atm, $K_p = \dfrac{4\alpha_1^2 P}{1-\alpha_1^2} = \dfrac{4 \times \alpha_1^2 \times (0.5)}{1-\alpha_1^2} = 0.141$; α_1=degree of dissociation

or $\quad 0.141(1-\alpha_1^2) = 2\alpha_1^2$, or $\alpha_1 = 0.257$ or 25.7%

Problem 4. At 1000°K for the equilibria,

(*i*) $CaCO_3 \rightleftharpoons CaO + CO_2$, $\qquad K_p = 4.0 \times 10^{-2}$ atm.

(*ii*) $C + CO_2 \rightleftharpoons 2CO_2$ $\qquad K_p' = 2.0$ atm.

Solid carbon, CaO and $CaCO_3$: are mixed and allowed to attain eqm. at 1000°K. What is the pressure of CO?

$$K_p = \frac{a_{CaO} \times a_{CO_2}}{a_{CaCO_3}} \approx P_{CO_2} \;;\; K_p' = \frac{a^2_{CO}}{a_C . a_{CO_2}} = \frac{P^2_{CO}}{P_{CO_2}}$$

$$\therefore K_p.K_p' = P^2_{CO} \quad \text{or} \quad P_{CO} = \sqrt{K_p.K_p'} = \sqrt{4 \times 10^{-2} \times 2.0} = 0.28$$

atmospheres.

Problem 5. N_2:H_2 mixture, (1 : 3) at 427°C and 20 atm. in eqm. contained 16% ammonia. Calculate K_p and K_c for

$$\tfrac{1}{2}N_2 + \tfrac{3}{2}H_2 \rightleftharpoons NH_3$$

For 100 moles mixture, there are 16 moles NH_3. Hence, every mole of mixture contains 0.16 mole NH_3, 0.63 moles H_2 and 0.21 moles N_2. Their partial pressures are

$$p_{NH_3} = \frac{0.16}{1} \times 20 \text{ atm.}\,; \quad p_{H_2} = \frac{0.63}{1} \times 20 \text{ atm.}\,; \quad p_{N_2} = \frac{0.21}{1} \times 20 \text{ atm.}$$

$$= 3.2 \text{ atm} \qquad = 12.6 \text{ atm} \qquad = 4.2 \text{ atm.}$$

$$\therefore\ K_p = \frac{P_{NH_3}}{p^{3/2}_{H_2} \cdot p^{1/2}_{N_2}} = \frac{3.2}{(12.6)^{3/2} \times (4.2)^{1/2}} = 3.49 \times 10^{-2}$$

$$K_c = K_p(RT)^{+1} = 3.49 \times 10^{-2} \times 700 \times 0.082 = 2.003$$

Problem 6. (*a*) At 400°C and 10 atm, 3.85% ammonia is present in eqm. with 1 : 3 mixture of N_2 and H_2. Calculate K_p for

$$N_2 + 3H_2 = 2NH_3$$

(*b*) At what pressure will 5% ammonia be available at this temperature? (*c*) What will be the percentage of ammonia if the pressure be 50 atmospheres?

The percentage of ammonia = 3.85, hence ($N_2 + H_2$) mixture would be 96.15%. That is $N_2 = \frac{1}{4} \times 96.15$, $H_2 = \frac{3}{4} \times 96.15$ percent.

$$\therefore\ K_p = \frac{p^2_{NH_3}}{p_{N_2} \cdot p^3_{H_2}} = \frac{(0.0385 \times 10)^2}{\frac{1}{4} \times 0.9615 \times 10) \times (\frac{3}{4} \times 0.9615 \times 10)^3}$$

$$= 0.000164$$

(*b*) $p_{NH_3} = 0.05P$; $p_{N_2} = \frac{1}{4} \times 0.95P$; $p_{H_2} = \frac{3}{4} \times 0.95P$

$$K_p = 0.000164 = \frac{(0.05P)^2}{(0.2375P)\,(0.7125P)^3} = \frac{0.0025P^2}{0.08594P^4}$$

$$\therefore\ P^2 = \frac{0.0025}{0.000164 \times 0.08594} = 177.5$$

$$\therefore\ P = 13.3 \text{ atm.}$$

(*c*) $p_{H_2} = 3p_{N_2}$; $p_{N_2} + p_{H_2} + p_{NH_3} = 50$ atm

$$p_{NH_3} = 50 - 4p_{N_2}\,; \quad p_{N_2} = \frac{50 - p_{NH_3}}{4}$$

$$K_p = 0.000164 = \frac{p^2_{NH_3}}{p_{N_2} p^3_{H_2}} = \frac{p^2_{NH_3}}{p_{N_2}(3p_{N_2})^3} = \frac{p^2_{NH_3}}{27p^4_{N_2}}$$

$$\therefore\quad \frac{p_{NH_3}}{p^2_{N_2}} = \sqrt{27 \times 0.000164}$$

or

$$\frac{p_{NH_3}}{\left(\frac{50 - p_{NH_3}}{4}\right)^2} = \sqrt{27 \times 0.000164}, \quad \therefore\quad p_{NH_3} = 7.52$$

But volume percent = mole-fraction × 100 = $\frac{7.52}{50.0} \times 100 = 15.04$

∴ Percentage of ammonia = 15.04%.

12.10. The Reaction Isotherm: Free Energy change in a Chemical Process

When a chemical change occurs spontaneously in a given set of conditions, it is a thermodynamical necessity that free energy would decrease. A correlation between the free energy change ($\triangle G$) and the eqm. constant of a chemical process can be easily derived.

Suppose at a temperature T and at a given set of arbitrarily chosen concentration (or pressures), the following reaction takes place.

$$a\text{A} + b\text{B} \rightarrow g\text{G} + h\text{H}$$

Let a moles of A react with b moles of B yielding g moles of G and h moles of H. The free energy change of this reaction at constant temperature and pressure would be

$$\triangle G = G_{produts} - G_{reactants} = g\mu_G + h\mu_H - a\mu_A - b\mu_B$$

where μ-terms are the respective chemical potentials or molar free energies.

Since $\mu = RT \ln a + \mu^0$ (Sec 11.7), we have

$$\triangle G = g[RT \ln a_G + \mu_G{}^0] + h[RT \ln a_H + \mu_H{}^0] - a[RT \ln a_A + \mu_A{}^0] - b[RT \ln a_B + \mu_B{}^0]$$

$$= RT \ln \frac{a_G{}^g \times a_H{}^h}{a_A{}^a \times a_B{}^b} + g\mu_G{}^0 + h\mu_H{}^0 - a\mu_A{}^0 - b\mu_B{}^0$$

or $$\triangle G = RT \ln \frac{a_G{}^g \times a_H{}^h}{a_A{}^a \times a_B{}^b} + Z \text{ (constant)} \qquad \text{. . . (XII.7)}$$

where a_G, a_H . . . etc. are the activities of the components in the given conditions. μ°-terms are the standard, and hence constant, chemical potentials.

The relation (XII.7) is valid for any chosen state and hence it would be valid also if we start with the components in the eqm. state. Using suffix ϵ for indicating eqm conditions.

$$\triangle G^\epsilon = RT\,ln \frac{a_{\epsilon G}^{g} \times a_{\epsilon H}^{h}}{a_{\epsilon A}^{a} \times a_{\epsilon B}^{b}} + Z = RT \ln K_a + Z \text{ . . . (eqn. XII.6)}$$

But at eqm., $\triangle G^\epsilon = 0$; hence $Z = -RT \ln K_a$

Thus for any chemical reaction, the free energy change,

$$\triangle G = -RT \ln K_a + RT \ln \frac{a_G{}^g \times a_H{}^h}{a_A{}^a \times a_B{}^b}$$

$$= -RT \ln K_a + RT\, \Sigma\nu \ln a \qquad \text{. . . (XII.8)}$$

This relation is commonly known as the *Reaction Isotherm.*

For ideal systems, the activities may be replaced by pressures or by concentrations. The equation (XII.8) may then be expressed as

$$\left.\begin{aligned} &\triangle G_p = -RT \ln K_p + RT\, \Sigma\nu \ln P \\ \text{or}\quad &\triangle G_c = -RT \ln K_c + RT\, \Sigma\nu \ln C \end{aligned}\right\} \quad \text{. . . (XII.9)}$$

If the reaction be carried out in such conditions that every product and reactant is maintained at unit pressure or at unit concentration, then $\Sigma \nu \ln P = 0$ and $\Sigma \nu \ln C = 0$. The free energy change in such condition is regarded as the standard free energy change, denoted by $\triangle G°$. Hence

$$\triangle G_p{}^0 = -RT \ln K_p \quad \text{and} \quad \triangle G_c{}^0 = -RT \ln K_c \qquad \ldots \text{(XII.10)}$$

Example 7. The standard free energy change in the formation of H_2S is -7.88 Kcal. Calculate K_p.

$$RT \ln K_p = -\triangle G^0 = +\,7.88 \text{ Kcal}$$

$$\therefore \qquad \log K_p = \frac{7880}{2.303 \times (1.98) \times 298} = 5.78$$

$$\text{or} \qquad K_p = 6.02 \times 10^5$$

12.11. Temperature dependence of Equilibrium constant

At a given temperature, the eqm. constant of a reaction remains unaltered, but its magnitude varies considerably with variation in temperature. To cite an example, the K_p-values of the reaction $N_2 + O_2 \rightleftharpoons 2NO$ is given here.

TABLE: K_p-VALUE OF $N_2 + O_2 \rightleftharpoons 2NO$ AT DIFFERENT TEMPERATURES

Temp. (°K)	2000	2200	2400	2500
$K_p \times 10^4$	4.08	11.00	25.10	36.00

A quantitative expression for the variation of eqm. constant with temperature can easily be deduced.

The reaction isotherm: $\triangle G = -RT \ln K_p + RT\, \Sigma \nu \ln P$

Differentiating with respect to temperature at *constant pressure*,

$$\left[\frac{d(\triangle G)}{dT}\right]_P = -RT\frac{d \ln K_p}{dT} - R \ln K_p + RT\frac{d\Sigma \nu \ln P}{dT} + R\Sigma \nu \ln P$$

The term $\Sigma \nu \ln P$ is a fixed quantity containing arbitrarily chosen pressures of the components, hence $\dfrac{d\,\Sigma \nu \ln P}{dT} = 0$. Multiplying both sides by T,

$$T\left[\frac{d(\triangle G)}{dT}\right]_P = -RT^2\frac{d \ln K_p}{dT} - RT \ln K_p + RT\Sigma \nu \ln P$$

$$= -RT^2\frac{d \ln K_p}{dT} + \triangle G$$

$$\text{Hence,} \qquad RT^2\frac{d \ln K_p}{dT} = \triangle G - T\left[\frac{d(\triangle G)}{dT}\right]_P \qquad \ldots \text{(XII.11)}$$

But from Gibbs-Helmholtz equation, $\triangle G - T\left[\dfrac{d(\triangle G)}{dT}\right]_P = \triangle H$

where $\triangle H$ is the heat-change (*i.e.*, heat of reaction) at temperature T.

$$\therefore \qquad RT^2 \frac{d\, ln\, K_p}{dT} = \triangle H$$

$$\therefore \qquad \frac{d\, lnK_p}{dT} = \frac{\triangle H}{RT^2} \qquad \text{. . . (XII.12)}$$

This is commonly known as the **van't Hoff equation,** which gives the variation of K_p with temperature T.

If the reaction be carried out at *constant volume*, a similar treatment would give the reaction,

$$\frac{d\, ln\, K_c}{dT} = \frac{\triangle U}{RT^2} \qquad \text{. . . (XII.3)}$$

This is often called the *reaction isochore.*

Integrating van't Hoff equation between the temperatures T_1 and T_2 when eqm. constants are K_{p_1} and K_{p_2}, we have, $(T_1 > T_2)$,

$$\int d\, ln\, K_p = \frac{\triangle H}{R} \int \frac{dT}{T^2}\, ; \quad \text{or} \quad ln\, K_p = \frac{-\triangle H}{R} . \frac{1}{T} + C$$

$$\text{or} \qquad ln \frac{K_{p_1}}{K_{p_2}} = -\frac{\triangle H}{R}\left[\frac{1}{T_1} - \frac{1}{T_2}\right] = \frac{\triangle H}{R}\left[\frac{T_1 - T_2}{T_1 T_2}\right] \qquad \text{. . . (XII.4)}$$

If the reaction be exothermic, *i.e.*, $\triangle H$ is $-ve$, then the expression on the right-hand is negative, hence $K_{p_1} < K_{p_2}$. It means that with rise of temperature, K_p will diminish, *i.e.*, resultants (at equilibrium) would be less. In other words, exothermic reactions are not favoured by rise of temperatures. If the reaction be endothermic, $K_{p_1} > K_{p_2}$ *i.e.*, endothermic reactions would be favoured by rise in temperature.

Problem 8. Calculate the enthalpy-change for the reaction $N_2 + O_2 \rightleftharpoons 2NO$ using the K_p-values given in the table (page 189) for temperature 2000°K and 2500°K.

$$\text{we have} \qquad K_{2000} = 0.000408 \quad \text{and} \quad K_{2500} = 0.00360$$

$$\therefore \qquad 2.303 \log \frac{K_{2500}}{K_{2000}} = \frac{\triangle H^\circ}{1.98} \times \left[\frac{1}{2000} - \frac{1}{2500}\right]$$

$$\text{or} \qquad 2.303 \log \frac{0.00360}{0.000408} = \frac{\triangle H^\circ}{1.98} \times \frac{500}{2500 \times 2000}$$

$$\text{whence} \qquad \triangle H^\circ = 43300 \text{ cal}$$

12.12. Le-Chatelier's Principle

How a system would behave if any of the parameter of the system at eqm. be altered was first enunciated by Le-Chatelier (1885) and Braun (1886). They made a generalisation that

If a system is in eqm., a change in any of the factors that determine the condition of eqm., will cause the equilibrium to shift in such a way as to minimize the effect of this change.

This is a general statement and qualitatively applicable to all systems to predict their behaviour when parameters are changed. We shall use this principle, which is sometimes called *the principle of mobile equilibrium*, to express the effects of pressure, temperature and concentration on chemical equilibria.

1. *Effect of change in temperature.* At eqm. two opposite reactions occur, one is exothermic and the other endothermic. Suppose the temperature of a system in eqm. is raised by supplying heat. According to Le-chatelier principle, the system will oppose the rise in temperature and will attempt to take away the applied heat. This is achieved by the system by causing more of the endothermic reaction of the system. Thus, if the temperature of the system,

$$N_2 + 3H_2 \rightleftharpoons 2NH_3,$$

in eqm. be raised the system would encourage the decomposition of ammonia ($2NH_3 \rightarrow N_2 + 3H_2$) which is endothermic and would absorb away the supplied heat. Similarly if the temperature be lowered, the loss of heat would be compensated by causing more of the exothermic process. Thus it can be categorically stated: *Increase of temperature favours endothermic processes and decrease of temperature favours exothermic processes.*

This is exactly what has been observed, in the previous section, from van't Hoff equation.

2. *Effect of change of pressure.* If the pressure on a system at equilibrium be increased, the system will try to get rid of the additional pressure. This is achieved by the system by reducing the volume. So, when pressure is increased, the equilibrium shifts in a direction in which the volume, and hence the number of moles, would diminish. Hence, in the eqm.

$$N_2 + 3H_2 \rightleftharpoons 2NH_3,$$

if pressure is increased, more of ammonia will be formed for, that will cause diminution in volume. In fact, we have seen in Sec. 12-6 page 181 that with rise in pressure more ammonia is obtained. Decrease of pressure will cause the system to change in the opposite direction, *i.e.*, ammonia will decompose to its elements.

It can be stated: *When the pressure of a system is increased, the eqm. is shifted in the direction that reduces the number of molecules in the system.*

For reactions, where the numbers of reactant and resultant molecules are equal, such as, $H_2 + I_2 \rightleftharpoons 2HI$, there is no volume-change, the change of pressure will have no effect on the equilibrium position.

3. *Effect of addition of a product.* Consider a system,

$$A + B \rightleftharpoons C + D$$

in equilibrium, to which a quantity of C is introduced.

Now, $$K_c = \frac{C_C \times C_D}{C_A \times C_B}$$

At a constant temperature, K_c remains constant, but C_c on the right hand side is increased. In consequence, the denominator must increase. In other words, some of the added C will react with D, to produce back A and B, in order to retain the constancy of K_c.

The addition of a product to a system in eqm. causes the eqm. to shift in the direction that decreases the concentration of the added component. For example,

(*i*) if some water is added to $BiCl_3$, the mixture turns milky due to the formation of BiOCl, as

$$BiCl_3 + H_2O \rightleftharpoons BiOCl + 2HCl$$

Now, if to this mixture at eqm. a little conc. HCl is added, the solution again becomes clear.

$$K_c = \frac{C_{BiOCl} \times C^2_{HCl}}{C_{BiCl_3} \times C_{H_2O}}$$

On addition of HCl, the numerator increases, so a backward reaction takes place, *i.e.* $BiCl_3$ is reformed, so that K_c remains constant.

(*ii*) To the dilute solution of $FeCl_3$, add a few drops of NH_4CNS. The mixture turns deep red due to the formation of $Fe(CNS)_3$.

$$FeCl_3 + 3NH_4CNS \rightleftharpoons Fe(CNS)_3 + 3NH_4Cl,$$

$$K_c = \frac{C_{Fe(CNS)_3} \times C^3_{NH_4Cl}}{C_{FeCl_3} \times C^3_{NH_4CNS}}$$

To the red solution, if excess of NH_4Cl be added, the red colour will gradually disappear and the pale yellow colour of $FeCl_3$ would reappear. That is, the reaction is thrown back, to keep K_c constant.

(*iii*) In the eqm., $PCl_5 \rightleftharpoons PCl_3 + Cl_2$, if Cl_2 is added, the partial pressure of Cl_2 will increase.

$$K_p = \frac{p_{PCl_3} \times p_{Cl_2}}{p_{PCl_5}}$$

As a result, to maintain K_p constant, PCl_5 must increase. That is, the added chlorine partially combines with PCl_3 to produce back PCl_5.

EXERCISES

I

1. What is a *reversible reaction*? Explain the terms 'equilibrium state' and 'equilibrium constant'. What attributes characterise a chemical equilibrium?

How can the dynamic nature of a chemical equilibrium be established?

2. State the Law of mass action. Give expressions for the mass law equilibrium of the following processes:

(*a*) $I_2 \rightleftharpoons I + I$; (*b*) $2NO_2 \rightleftharpoons N_2O_4$; (*c*) $3Fe + 4H_2O \rightleftharpoons Fe_3O_4 + 4H_2$;
(*d*) $NH_4HS\ (s) \rightleftharpoons NH_3\ (g) + H_2S\ (g)$

3. Discuss, on the basis of mass action law, the influence of pressure on the following gaseous equilibria:

(*a*) $PCl_5 \rightleftharpoons PCl_3 + Cl_2$ (*b*) $H_2 + Br_2 \rightleftharpoons 2HBr$ (*c*) $N_2O_4 \rightleftharpoons 2NO_2$ (*d*) $CO + Cl_2 \rightleftharpoons COCl_2$

4. Derive thermodynamically the expression for the eqm. constant of the reaction,

$$N_2 + 3H_2 \rightleftharpoons 2NH_3$$

5. Establish the relation between K_p and K_c of a gaseous system. Can you predict when K_p would be greater than K_c ?

At 400°C, the value of K_p, for the reaction $\frac{1}{2}N_2 + \frac{3}{2}H_2 \rightleftharpoons NH_3$, is 0.013 atm. Calculate K_c.

[Ans. 0.713]

6. Show that for the gaseous reaction, $2H_2S \rightleftharpoons 2H_2 + S(g)$, the eqm. constant,

$$K_p = \frac{\alpha^3 P}{(2+\alpha)(1-\alpha)}\text{, where } \alpha = \text{degree of disociation.}$$

7. Derive an expression for the free energy change during an isothermal chemical process. How is standard free energy change related to the eqm. constant?

8. What is chemical equilibrium? Illustrate it with instances of chemical process in liquid systems and in heterogeneous systems.

9. State Le Chatelier's principle. Discuss with the help of this principle the effect of pressure and temperature on the following equilibria:

$N_2 + 3H_2 \rightleftharpoons 2NH_3$; $\Delta H = -23.0$ Kcal

$N_2 + O_2 \rightleftharpoons 2NO$; $\Delta H = +43.0$ Kcal

$C_6H_6(g) + 3H_2 \rightleftharpoons C_6H_{12}(g)$; $\Delta H = -46.0$ Kcal

10. How is the equilibrium constant of a chemical process quantitatively related to temperature? Deduce the relation.

11. What will be effect of adding some amount of argon (*i*) at constant volume and (*ii*) at constant pressure to the following systems at eqm?

(*a*) $PCl_5 \rightleftharpoons PCl_3 + Cl_2$

(*b*) $N_2 + 3H_2 \rightleftharpoons 2NH_3$

(*c*) $H_2 + I_2 \rightleftharpoons 2HI$

12. Discuss the effect of addition of a product of a chemical process to the system at eqm.

13. Make critical comments on the following statements:

(*a*) At eqm. the chemical reaction stops

(*b*) The synthesis of exothermic compounds is fovaoured at higher temperatures

(*c*) A mixture of H_2, O_2 and H_2O-vapour does not change in composition even if kept for several days at room temperature. The system therefore has attained chemical equilibrium.

(*d*) The numerical values of K_p and K_c for all gaseous reactions shall always differ.

14. At 100°C, the vapour density of nitrogen tetroxide is 25 at 1 atm. Show that $K_p = 9.6$.

15. At 427°C, for the gaseous reaction. $H_2 + I_2 \rightleftharpoons 2HI$; $K_p = 55.3$. What weight of HI will be formed at eqm. if 1 mole of H_2 and 1 mole of I_2 be placed in a litre vessel at 427°C? [Ans. 100.7 gm]

16. At 150°C and 1 atm., TCl_5 is 60% dissociated. Find its dissociation constant. [Ans. 0.56]

17. At 770°K and a total pressure of 261.4 mm, N_2O_4 is 63% dissociated. What would be its extent of dissociation under a pressure of 93.8 mm at the some temperature? [Ans. $\alpha = 0.804$]

18. At 1000°C, the pressure of iodine gas is found to be 0.112 atm., whereas the expected pressure is 0.074 atm. The increased pressure is due to the dissociation, $I_2 \rightleftharpoons 2I$. Calculate K_p. Also find out the pressure at which I_2 would be 90% dissociated at 1000°C.

[Ans. $K_p = 15.2 \times 10^{-2}$; $P = 8.9 \times 10^{-2}$ atm]

19. At 127°C, for the reaction, $SO_2Cl_2 \rightleftharpoons SO_2 + Cl_2$, $K_p = 2.4$ in atmospheres. 6.75 gm SO_2Cl_2 are placed in an empty 1 litre bulb and the temp. is kept at 127°C. What would be the pressures of SO_2, SO_2Cl_2 and Cl_2? [Ans. $P_{so_2} = P_{cl_2} = 1.118$ atm, $P_{so_2cl_2} = 0.522$ atm]

20. In a phosgene reaction at 400°C, the initial pressures are $P_{CO} = 342$ mm, $P_{Cl_2} = 352$ mm. The total pressure at eqm. is 440 mm. $CO + Cl_2 \rightleftharpoons COCl_2$

Calculate the percentage dissociation of phosgene at 400°C and 1 atm. [Ans. 20.6%]

21. Ammonia gas in eqm. with 1:3 nitrogen-hydrogen mixture at 50 atm. and 400°C is 20 percent by weight. Calculate the equilibrium constant. (Cal. Univ.) [Ans. $K_p = 8.6 \times 10^{-3}$]

22. At 49.7°C, the value of K_c is 8.55×10^{-3} moles/litre for the reaction, $N_2O_4 \rightleftharpoons 2NO_2$. Calculate K_p. [Ans. 0.0227]

23. For the reaction $N_2 + O_2 \rightleftharpoons 2NO$, free energy change is given by $\Delta G^\circ = 22000 - 2.5T$. Calculate K_p at 2000°K. [Ans. 0.014]

24. The dissociation constant of $CaCO_3$ at 900°C and 1000°C are 790 mm and 2940 mm. Calculate the heat of dissociation in this temperature range. [Ans. 39.65 Kcal]

25. For the reaction $2NO \rightleftharpoons N_2 + O_2$, the K_p-value at 2000°K is 4.08×10^{-4} atm. The heat of dissociation is -26 Kcal. Calculate K_p at 3000°K. [Ans. 36×10^{-7} atm]

26. In a reaction, $X_2 + Y_2 \rightleftharpoons 2XY$, at a temperature of 45°C, there were produced at eqm. 3.70 moles of XY from 2.06 moles of X_2 and 3.19 moles of Y_2. Calculate the eqm. constant.

If at 55°C, the eqm. constant were 30, calculate the heat of reaction. (Lucknow Univ.)
[Ans. $K = 48.7$, $\Delta H = -10.09$ Kcal]

27. Two moles of PCl_5 are heated in a closed 2-litre vessel. When equilibrium is attained, it is 40% dissociated into PCl_3 and Cl_2. Calculate the eqm. constant. (Punjab Univ.)
[Ans. $K = 26.7 \times 10^{-2}$ moles/litre]

28. Calculate the dissociation constant of the reaction, $2CO_2 \rightleftharpoons 2CO + O_2$ if the degree of dissociation of CO_2 at 1 atm. is 40%. (Kurukshetra Univ.) [Ans. $K_p = 7.4 \times 10^{-2}$]

CHAPTER 13

SOLUTIONS : GENERAL BEHAVIOUR AND PHYSICAL EQUILIBRIA

13.1. Solutions

A solution is defined as a homogeneous mixture of two or more substances. Since the mixture is homogeneous, it has the same composition and properties at every point of the system. In other words, *the solution is a single phase system of two or more components, the proportion of the components being the same throughout.* The component which is present in the largest proportion is called the *solvent* and the other components are called *solute s.*

Of the different types of solution, the following are of interest:

(*i*) Solutions of gases in gases
(*ii*) Solutions of gases in liquids
(*iii*) Solutions of liquids in liquids
(*iv*) Solutions of solids in liquids
(*v*) Solutions of solids in solids

These will be separately discussed in the following pages.

13.2. Modes of expression of Composition of Solutions

The relative amount of a substance present in a solution or a mixture is known as its *concentration.* In dealing with physico-chemical phenomena, there are three different widely used ways of expressing concentration.

(*i*) *Molarity*: The molarity (M) of a solution is the number of gm-moles of the solute present in 1 litre of the solution. A $0.1M$ $CaCl_2$ solution contains one-tenth gm-mole of the salt in one litre of the solution; the conc. of Ca^{++} is $0.1M$ and the conc. of Cl^- is $0.2M$, assuming complete dissociation.

(*ii*) *Molality*: The molality (m) of a solution is the number of gm-moles of the solute present in 1000 *gm of the solvent.* A $0.1m$ urea solution in alcohol means one-tenth of a gm-mole of urea dissolved in 1000 gm of alcohol.

(*iii*) *Mole-fraction*: In this system, the relative amount of a component in a mixture is expressed as a fraction of the total amount of all the components, the amounts of every component being measured in gm-molecules. To illustrate: suppose in a solution there are present, n_1 gm-moles of A and n_2 gm-moles of B, *i.e.*, total amount is $n_1 + n_2$ gm-moles. Then,

$$\text{the mol-fraction of component } A = \frac{n_1}{n_1+n_2} = x_1 \text{ (say)}$$

$$\text{and the mol-fraction of component } B = \frac{n_2}{n_1+n_2} = x_2 \text{ (say)}$$

So that, $x_1 + x_2 = 1$

Generally speaking, if there are *i*-components present in the solution, then

$$x_1 = \frac{n_1}{n_1+n_2 \ldots +n_i} = \frac{n_1}{\Sigma n_i}; \quad x_2 = \frac{n_2}{\Sigma n_i}; \text{ etc.}$$

Hence, the sum of the mol-fractions of all the *i*-components will be,

$$x_1 + x_2 + x_3 + \ldots = 1$$

I. SOLUTION OF GASES IN GASES

13.3 All gases mix freely and spontaneously in all proportions forming uniform homogeneous mixtures. The total pressure (P) exerted by the gas-mixture is the sum of the individual partial pressures (p_a, p_b, ...) of the components.

$$P = p_a + p_b + \ldots$$

This is the Dalton's Law of partial pressures already discussed in Sec. 1.7. and Sec. 2.5.

If at a temperature T, n_1, n_2, n_3 ... moles of several gases be present in a vessel of volume v, then

$$p_1 = n_1RT/v, \; p_2 = n_2RT/v, \quad p_3 = n_3RT/v, \ldots$$

Hence, the total pressure P,

$$P = p_1 + p_2 + p_3 + \ldots \quad = \frac{RT}{v}(n_1 + n_2 + n_3 \quad \ldots)$$

or $$P = n\frac{RT}{v}$$

∴ The partial pressures are

$$p_1 = \frac{n_1}{n}P = x_1P, \text{ where } x_1 \text{ is its mol-fraction}$$

Similarly $p_2 = \frac{n_2}{n}P = x_2P; \quad p_3 = \frac{n_3}{n}p = x_3P; \quad \ldots$

The partial pressure of a component in a gas-mixture is given by the product of the total pressure and its mol-fraction.

The mixing of gases is spontaneous and hence it always leads to a net increase in entropy. This is due to the fact that randomness is much increased.

II. SOLUTION OF GASES IN LIQUIDS

13.4. Solubility of Gases

The solubility of different gases in different liquids vary with the nature of the gas and the solvent. It is usually seen that gases which tend to associate with the solvent or which ionise on dissolution are higly soluble. That is why the solubility of ammonia and hydrogen chloride in water is so large. The so called permanent gases like O_2, N_2, He, etc. are only slightly soluble.

The solubility of a gas is the maximum volume of the gas dissolved by 1 c.c. of the given solvent at the given temperature and pressure.

But the solubility of a gas in a liquid is often expressed in terms of *absorption coefficient* (α) which is defined as the volume of the gas in c.c. (reduced to N.T.P.) dissolved in 1 c.c. of the liquid at the given temperature, when partial pressure of the gas is 760 mm.

SOLUBILITY OF GASES (ABSORPTION COEFFICIENT)

Gases	*In wates*		*In ethyl alcohol*	
	α_0°	α_{25}°	α_0°	α_{25}°
CO_2	1.713	0.759	4.44	2.79
N_2	0.0232	0.0147	—	0.1312
O_2	0.0489	0.0285	0.2337	0.2171
H_2	0.0215	0.0178	—	—

13.5. Henry's Law

The solubility of a gas in a liquid depends upon the pressure and the temperature. Le-Chatelier's principle predicts that with increase in pressure the volume would diminish. This is possible from more gas being dissolved, *i.e.*, the solubility will increase with rise in pressure. It is indeed found to be true.

William Henry (1803) made a systematic investigation of the solubility of gases in liquids and established that *the mass of gas* (m) *dissolved by a unit volume of a given liquid is proportional to the pressure* (p) *of the gas at a constant temperature.*

i.e., $$m/p = \text{constant} = K_1 \qquad \ldots \text{(XIII.1)}$$

This is 'Henry's Law'. Now the mass of gas (m) dissolved in unit volume is proportional to its conc. (c_2) in solution, whereas the pressure (p) of the gas is given by $p = c_1RT$, c_1 is the concentration in the gas phase.

Hence $$K_1 = \frac{m}{1} = \frac{k'c_2}{c_1RT}$$

or, at constant temp., $$\frac{c_2}{c_1} = K_2\,(\text{constant}) \qquad \ldots \text{(XIII.2)}$$

That is, *at a constant temperature, the concentrations in the gas and solution phases bear a constant ratio to one another.*

If v be the volume of the gas dissolved per unit volume of the solution, then $m = (M/RT).pv = zpv$, where z is a constant.

So, $$K_1 = \frac{m}{p} = \frac{zpv}{p} \quad \text{or,} \quad v = (K_1/z) = \text{constant.}$$

Hence, *the volume of a gas absorbed in unit volume of a given liquid is independent of pressure.*

These are the different ways in which the Henry's Law is stated. It should however be mentioned that the law is strictly applicable only to dilute solutions and ideal systems.

In soda-water, lemonade, etc. there is dissolved carbon dioxide under pressure. On releasing the pressure, the dissolved gas comes out as its solubility decreases with lowering of pressure. This is a common illustration of the Henry's Law. The study of the solubility of gases under different pressures in blood or lipid fats is of considerable importance owing to their physiological importance for deep-water divers and mountaineers.

The influence of temperature on solubility may also be easily found out. In general, the solubility of a gas in a liquid decreases with rise in temperature. It is thus an exothermic process. An exothermic process is favoured at lower temperature (Le Chatelier) and hence gas-solubility will be less at higher temperatures. At a given pressure p, if m_1 and m_2 be the masses of gas dissolved per unit volume of the liquid, at temperatures T_1 and T_2°K, then,

$$m_1/p = K_1 \quad \text{and} \quad m_2/p = K_2$$

$$\therefore \qquad \frac{K_1}{K_2} = \frac{m_1}{m_2} = \frac{C_1}{C_2}; \quad (C_1, C_2 \text{ are concentrations})$$

If $\triangle H$ be the heat-change in the process of solution, supposed to be constant, then applying the isochore-relation, we have

$$ln\frac{K_1}{K_2} = -\frac{\triangle H}{R}\left[\frac{1}{T_1} - \frac{1}{T_2}\right], \text{ or } ln\frac{C_1}{C_2} = -\frac{\triangle H}{R}\left[\frac{1}{T_1} - \frac{1}{T_2}\right] \qquad \ldots \text{(XIII.3)}$$

This is the quantitative relation between Henry's Law constant and temperature.

III. SOLUTION OF LIQUIDS IN LIQUIDS

13.6. Miscibility of Liquids

When water is added to alcohol, the two liquids are completely miscible in any proportion and form a homogeneous solution. When water is added to, say, nitrobenzene scarcely any nitrobenzene will dissolve in water or any water in nitrobenzene. The two liquids will exist in separate layers; the liquid pair is immiscible. But if we add some phenol to water, first phenol will be dissolved in water but as the amount of added phenol increases, phenol will form a separate layer. In fact the water layer will contain dissolved phenol and the phenol layer will also have appreciable amount of dissolved water. Such liquids are *partially miscible.* When two such partially miscible liquids (A & B) are brought together in appreciable amounts we have two saturated solutions in two layers—one of A in B and another of B in A—in equilibrium. These two solutions are described as **conjugate solutions.**

The liquid-liquid systems are studied under three categories;

(*i*) Partially miscible liquid pairs

(*ii*) Completely miscible liquid pairs

(*iii*) Immiscible liquid pairs

PARTIALLY MISCIBLE LIQUID PAIRS

The study of partially miscible liquid pairs has revealed that there are three types of such systems. Some partially miscible liquid pairs become completely miscible at and above a certain high temperature; while there are others which become completely miscible at or below a certain low temperature. There is a third type of liquid pairs which become miscible both above certain high temperature as well as below some low temperature. These may be illustrated with typical examples. The studies are made by observing the variation of solubilities or concentrations with temperature, *i.e.* t-c curves.

13.7. Type I: Phenol and Water. In Fig. XIII.1, *AB* is the solubility curve of phenol in water. It gives the percentage of phenol dissolved in water at different temperatures, the solubility rising with temperature. On the other hand when water is added to phenol slowly, small amounts of water are immediately dissolved but when the amount of added water is increased, the limit of saturation is reached and water forms a separate layer. The solubility curve of water in phenol is given by *CB*, the solubility again increasing with temperature. The two solubility curves meet smoothly at *B* (temp. 66°C, 33% phenol).

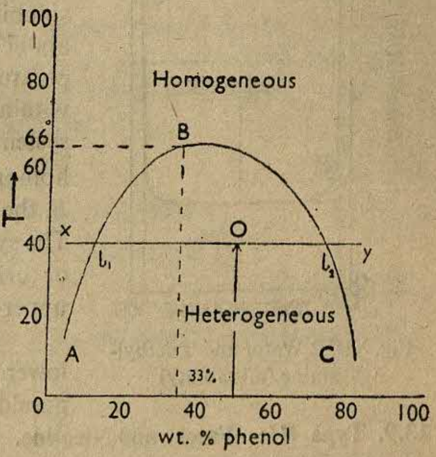


Fig. XIII-1. Water and phenol (miscibility)

At a given temperature (say 40°C), if we have *x* percent phenol in water, it will be completely miscible and a homogeneous solution will result. Keeping the temperature constant, if we go on increasing the amount of phenol, the solubility limit l_1 will be reached. Any further addition of phenol will give rise to two separate layers: (*i*) water in phenol layer and (*ii*) phenol in water layer. On the left of l_1, a point will correspond to homogeneous solution and on its right a point would indicate hetrogeneous system of two layers or phases. *AB* is thus the boundary line between homogeneous and hetrogeneous existence of the system. Similarly if water is added in small amounts to phenol such that phenol is *y* percent, it would fully dissolve producing homogeneous solution of water in phenol. Further addition of water will lead to the point l_2 of limiting solubility, on the left of which two hetrogeneous phases of conjugate solution would appear. So BC is the boundary on the left of which it is hetrogeneous and on the right homogeneous. That is, any point within the area ABC will correspond to the heterogeneous system and any point outside ABC will represent homogeneous or completely miscible system.

It is thus seen that at any temperature above that of B the two liquids would be miscible in all proportions. This temperature above which complete miscibility at all proportions takes place is called *upper consulate temperature or critical solution temperature* (*C.S.T.*) of the given system.

There are other liquid pairs which behave like phenol-water system showing upper C.S.T., such as,

(*i*) Aniline/hexane (t = 59.6°C)
(*ii*) CS_2/CH_3OH (t = 40.5°C)
(*iii*) Bi/Zn (t = 850°C)
(*iv*) Aniline/H_2O (t = 167°C)

13.8. Type II: Water and Triethylamine. The *t-c* diagram of the mutual solubilities of these two liquids is given in Fig. XIII.2. *AB* is the solubility curve of triethylamine in water and *CB* that of water in triethylamine. In both the cases, the solubilities decrease with rise in temperature. The two solubility curves become almost horizontal at about 18.5°C and practically merge at this temperature. As in the previous case, any point within *ABC* corresponds to heterogeneity of the system while outside *ABC*, the system would be homogeneous. Below the temperature of that of *B*, the two liquids are miscible in all proportions. The system has thus a *lower consolute temperature* or critical solution temperature instead of an upper one.

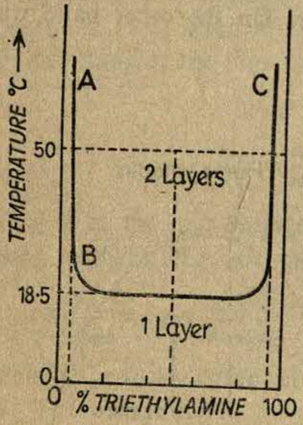


Fig. XIII.2 Water and Triethylamine (miscibility)

There are other liquid pairs which have lower critical solution temperatures such as: paraldehyde/water; diethylamine/water, etc.

13.9. Type III: Water and Nicotine. There are cases where the mutual solubility curve is a closed one having both an upper critical solution temperature and a lower critical solution temperature. Such is the system of water and nicotine. The miscibility curves of this pair are represented in Fig. XIII.3. Above 208°C as also below 61°C, the two liquids are miscible in all proportions. These are the upper and the lower critical solution temperatures. In between these two temperatures with appreciable amounts of the components there would occur heterogeneous phases of two conjugate solutions. Other systems of this type are:

(*a*) Methyl ethyl ketone/water (133°/−6°C)
(*b*) Gycerol/m-toluidine (120°/7°C)

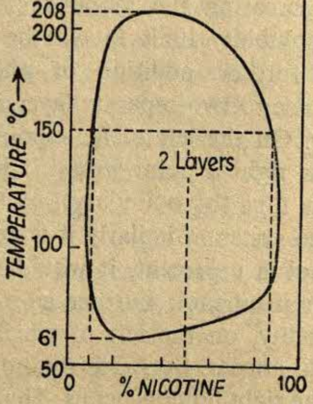


Fig. XIII.3. Water and Nicotine (miscibility)

COMPLETELY MISCIBLE LIQUID PAIRS

13.10. Vapour Pressure of Binary liquid mixtures: Raoult's Law

From an extensive study of the vapour pressure of different solutions of non-volatile solutes, Raoult (1886) established that

The vapour pressure (P_1) over a solution is equal to the vapour pressure ($P_1°$) of the pure solvent multiplied by the mol-fraction (x_1) of the solvent in the solution;

$$P_1 = x_1 P_1^0 \qquad \ldots \text{(XIII.4)}$$

This is known as the **Raoult's Law**: It is quite satisfactory when dilute solutions are used.

If the solute be a volatile component, the Raoult's Law will hold good provided the components behave *ideally*. In this case, the total pressure will be the partial pressures of the two components:

$$p_1 = x_1 P_1^0, \qquad p_2 = x_2 P_2^0$$

[The suffix 1 is used for solvents and 2 for solutes]

Consider a liquid pair *A* and *B* which are volatile and completely miscible and form an ideal mixture with mol-fractions x_A and x_B. Their vapour pressures in the pure state are P_A^0 and P_B^0. If p_A and p_B denote the partial vapour pressures of the two components in the vapour over the solution, then

$$p_A = x_A P_A^0 \qquad p_B = x_B P_B^0 \qquad \ldots \text{(XIII.5)}$$

The total vapour pressure (P) of the solution; $P = p_A + p_B$

i.e., $$P = x_A P_A^0 + x_B P_B^0 = (1 - x_B) P_A^0 + x_B P_B^0$$

or $$P = P_A^0 + (P_B^0 - P_A^0)\, x_B \qquad \ldots \text{(XIII.6)}$$

It is obvious that P_A, P_B or total pressure P plotted against mol-fraction of either component, say x_A, would yield linear graphs as in Fig. (XIII.4).

In this figure, the solid lines represent the partial pressures of *A* and *B*. The dashed line is the total pressure of the solution at different concentrations. When $x_B = 1$, pure *B* is present, $P = P_B^0$; when $x_B = 0$ pure *A* is present, $P = P_A^0$. And at the conc. $x_B = S$, the total pressure $SP = SR + SQ$.

The equation (XIII.6) gives the relation between vapour pressure and the composition of *solutions*. At eqm., the liquid phase and the vapour phase compositions are not the same.

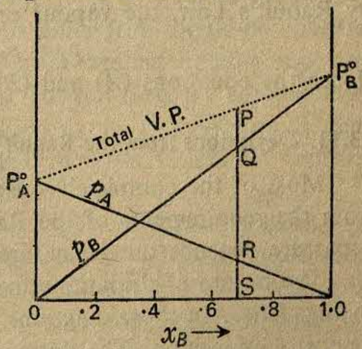


Fig. XIII.4. Vap. Pressures of ideal solutions

Composition of solution and vapour phases (Ideal systems)

Suppose x_A, x_B are the mol-fractions of A and B in the liquid phase and x'_A, x'_B are their mol-fractions in the vapour phase. Then,

by Dalton's law: $p_A = Px'_A$ and $p_B = Px'_B$

by Raoult's law: $p_A = P_A^0 x_A$ and $p_B = P_B^0 x_B$

where P = total pressure, $P_A{}^0$, $P_B{}^0$ are the vapour pressures of components in the pure state.

$$\therefore \quad \frac{P_A}{P_B} = \frac{x'_A}{1-x'_A} \quad \text{and hence}$$

$$x'_A = \frac{x_A P_A{}^0}{x_A P_A{}^0 + x_B P_B{}^0}$$

$$\therefore \quad \frac{x'_A}{x_A} = \frac{P_A{}^0}{x_A P_A{}^0 + x_B P_B{}^0}.$$

This is the ratio of mol-fractions of A in the vapour and liquid. Remembering $x_A + x_B = 1$, we find

(*i*) If $P_B{}^0 > P_A{}^0$, x'_A will be less than x_A. There is larger amount of A in the liquid than in the vapour.

(*ii*) If $P_A{}^0 > P_B{}^0$, x'_A will be greater than x_A. There will be more of A in the vapour than in the liquid.

It is thus seen that for ideal solutions, the vapour contains more of the component which has a higher vapour pressure and hence lower normal boiling point.

Ideal Solutions: Raoult's Law is valid for ideal solutions. In fact, ideal solutions have been conceived on the basis of the Raoult's Law. A solution is regarded as ideal if each component obey Raoult's Law over the entire range of composition; *i.e.* $p_i = x_i p_i{}^0$.

Beside this, ideal solutions are also characterised by the fact that during mixing there would be no net enthalpy-change or volume-change.

$$\triangle H_{\text{mix}} = 0 \qquad \triangle V_{\text{mix}} = 0$$

Raoult's Law and Henry's Law: By Henry's Law, the weight of gas (w_2) dissolved per unit volume at pressure p_2 is given by, $w_2 = k'p_2$. But in very dilute solutions w_2 is proportional to its mol-fraction x_2, hence, $w_2 = k''x_2$. Substituting

$$x_2 = kp_2, \quad \text{or} \quad p_2 = k_2 x_2 \qquad \ldots (A)$$

By Raoult's Law, the vapour pressure of the volatile solute (ideal),

$$p_2 = p_2{}^0 x_2 \qquad \ldots (B)$$

Hence the equations (A) and (B) are identical; $k_2 = p^0{}_2$,

13.11. Deviations from the Raoult's Law

Most of the completely miscible liquid pairs show a considerable departure from the requirements of the Raoult's Law and hence non-ideal. The extent of departure depends on the nature of the liquids and on concentration.

The nature of deviations from the Raoult's Law is of *three types* as shown in Fig. III. 5. In these diagrams, the total and partial vap. pressures are plotted against composition. The dotted lines correspond to Raoult's Law requirements and broad lines are experimental observations.

(*i*) In **Type I** are systems in which total vap. pressure is continuous and at any composition, it is intermediate between the vap. pressures of the two pure components (Fig. *a*). Such systems are called **Zeotropic Mixtures.**

Examples: water-methylal, benzene-toluene, CCl_4-C_6H_6, etc.

(*ii*) In **Type II** are the systems in which the deviations from the Raoult's Law are positive. The vapour pressure rises to maximum and then falls with change in composition. The maximum vapour pressure is higher than the vapour pressure of either pure component (Fig. *b*). The vap. pressure of a particular composition is maximum. If one component shows positive deviation, the other also exhibits the same. Such systems are called **Azeotropic Mixtures with maximum vapour pressure (or minimum b. pt.)**

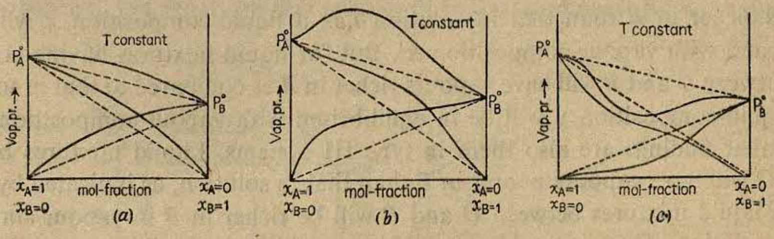


Fig. XIII.5. (*a*) Zeotropic mixture (*b*) Azeotropic mixture with maximum vap. pr. (*c*) Azeotropic mixture with minimum vap. pr.

Examples: CH_3OH-CS_2, C_6H_6-Cyclohexane, H_2O-C_2H_5OH, $(CH_3)_2CO$-CS_2, etc.

(*iii*) In **Type III** the systems show negative deviation from the Raoult's Law [Fig. *c*]. They exhibit a minimum vapour pressure for a particular composition and it is below the vapour pressure of either pure component. Both the components individually also exhibit negative deviation. These systems are called **Azeotropic Mixtures with minimum vapour pressure (or maximum b. pt.)**

Example: H_2O-HNO_3, $(CH_3)_2CO$-$CHCl_3$, pyridine-acetic acid etc.

In the diagrams in Fig. XIII.5, the vapour pressures are plotted against liquid compositions. At eqm., the vapour-compositions differ from liquid-compositions. In Fig. XIII.6, the vapour-pressures are given both against liquid-compositions and vapour-compositions for all the three types. In each case, the liquid composition-curve (*L*) is above the vapour-composition curve (*V*). A and B denote vapour-pressures of pure components. The point O in types II and III represents the maximum or minimum point.

Vapour Pressure vs. Composition: In type I the vapour-composition and liquid-composition curves are both continuous and at all concentrations the composition in the two phases are different. A liquid-mixture of composition *x* will be in equilibrium with vapour mixture of composition *x'*. Obviously, the vapour will be richer in the component which is more volatile.

In the other two types (II and III), the vapour-composition curve touches the liquid-composition curve at the maximum or the minimum points. This means that a liquid-mixture with composition corresponding to the maximum or minimum point (*O*) will be in equilibrium with a vapour-phase of the same composition; the compositions of the vapour and solution are identical. The diagrams of types II and III are thus made up to two portions: namely (*i*) one between pure component *A* and a solution of maximum or minimum vap-pressure and (*ii*) the other between pure component *B* and a solution of maximum or minimum vapour pressure.

In type II liquid mixtures having composition between *A* and *O* will have vapours richer in *B* than that in solution *i.e.*, a liquid-composition *x* will be in equilibrium with vapour-composition *x'*. But for liquid mixtures having compositions between *O* and *B* will have vapours richer in *A* as compared to that in solution. So a liquid-composition *y* will be in equilibrium with vapour-composition *y'*.

Similar findings are also there in type III systems. Liquid mixtures between *A* and *O* will have vapours poorer in *B* than that in solution, as indicated by *x* and *x'*. But liquid mixtures between *O* and *B* will be richer in *B* in vapour state than that in solution. Thus, a liquid composition *y* will be in equilibrium with vapour composition *y'*.

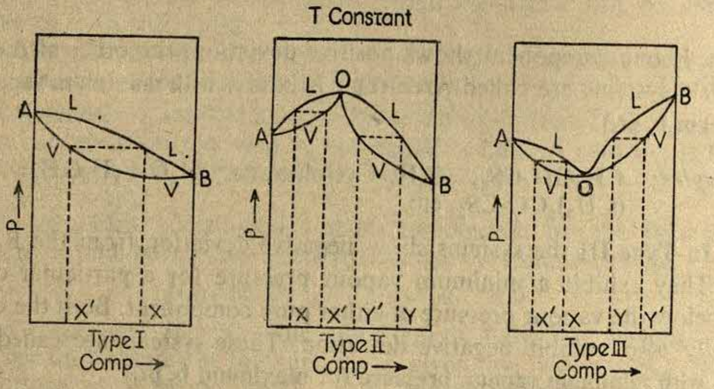


Fig. XIII.6. Vap. pressures against liquid compositions and vapour compositions.

13.12. Boiling Point—Composition diagrams

The *boiling-point of a liquid mixture* is the temperature at which the total vap.-pressure becomes equal to the external pressure.

With the variation in composition the vapour pressure of a mixture of two liquids changes. The higher the vapour pressure of a mixture the lower will be its boiling point. Thus, a liquid mixture of type II which has the composition corresponding to maximum vapour pressure will have a minimum boiling point compared to mixtures with any other composition. In other words, if at a fixed pressure, the boiling pt-composition diagrams are prepared, these will be inverted in shape in relation to vapour pressure-composition diagrams. The boiling point-composition diagrams for all the three types of liquid mixtures are discussed below. These diagrams have a direct bearing on the possibility of separating the components of miscible binary liquids. The three types may be considered separately.

(*i*) **Boiling pt-Composition Diagram with no Maximum or Minimum. Zeotropic System.** In Fig. XIII.7 *ALB* is the b.pt.-liquid-composition curve and *AKB* represents the b. pt.-vapour-composition curve. A liquid mixture, having a composition *x* will boil at $t°_1$ and the vapour in equilibrium with the liquid will have the composition *y*; the b. pt decreases with increase in conc. of *B*. If this vapour be removed and condensed the liquid will have the same composition y. If this condensed liquid be boiled again, it will boil at $t_2°$ and the vapour in eqm. will have composition z. On removing this vapour and condensing, a liquid of composition z will be obtained. On repeating this process of boiling and condensing in successive

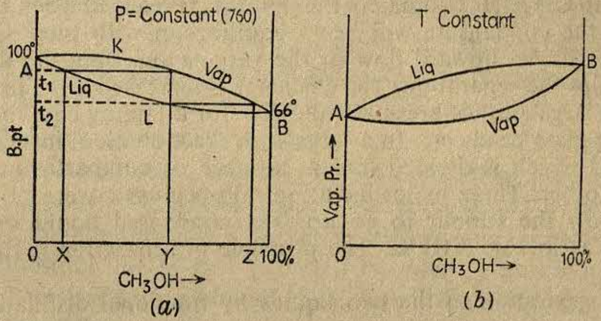


Fig. XIII.7. (*a*) B.pt. composition diagram (*b*) Vap-Pr.-composition diagram (Type I system) H_2O/CH_3OH

fractions, ultimately the pure component B would be obtained. In the residual liquids the component A would gradually be increasing. The two liquids can thus be separated from such a mixture of type I. The tedious process of successive evaporation and condensation is in practice avoided by using a fractionating column in distillation.

Fractional distillation. A common fractionating column used in laboratory is a fairly long glass tube fitted vertically above the distilling flask and packed with glass beads (Fig. XIII.8). When the liquid mixture boils, the vapour rises up in the column and progressively cools as it goes higher and higher. Suppose we start with H_2O-CH_3OH mixture in the flask having about 10% methylal. It would boil

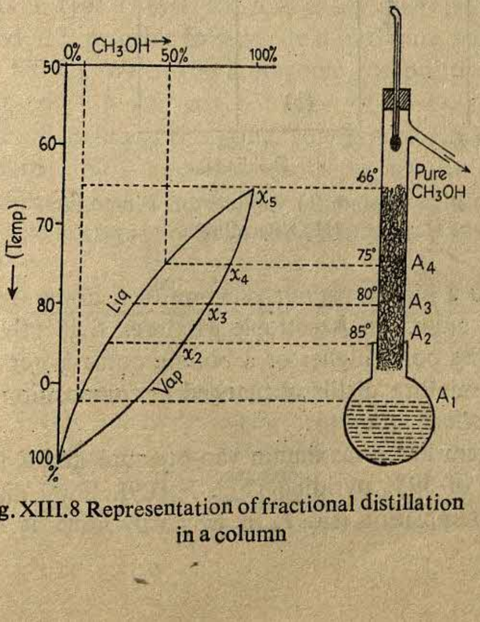


Fig. XIII.8 Representation of fractional distillation in a column

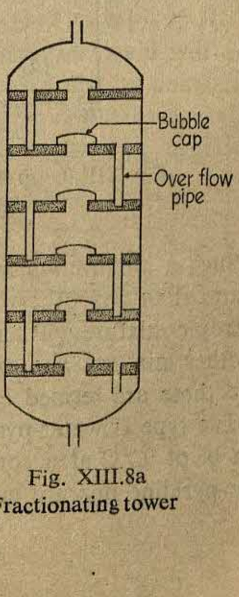


Fig. XIII.8a
Fractionating tower

at about 92°C, the vapour having the composition x_1. When this vapour goes up in the column, at the point A_2 a portion will condense and the vapour (say at 85°C) will have the composition x_2. As more hot vapour goes up, this condensed liquid boils and at the point A_3 (relatively cooler) a condensate is obtained (say at 80°C) in eqm. with a vapour having composition x_3. In its turn this liquid will also boil when higher temperature vapours come up from below producing vapours richer in CH_3OH. Ultimately the point A_5 is reached when the temperature is 66° or less, the condensate will be in equilibrium with pure CH_3OH, which is easily separated. An upward flow of the vapour and opposite downward flow of the liquid helps the separation. The efficiency is increased if the process is carried out slowly and large surface areas are allowed for attaining equilibria at different points by using glass beads etc. In a large scale fractionation, instead of a column a tower is used which is divided into a number of compartments by plates set one above the other. These plates have central openings covered by loose bubble caps which allow the vapour to go up. The condensed liquid drops down by overflow pipes as in Fig. XIII.8a. The principle of separation is the same.

Complete separation of the two liquids by fractional distillation is possible only in type I mixtures where the vap-pressure progressively changes from that of one component to that of the other component. Liquid air being such a mixture, it is possible to obtain pure oxygen and pure nitrogen by fractional distillation.

(*ii*) **Boiling point-Composition Diagram with a Minimum.** In type II liquid pair systems, the vapour pressure reaches a maximum for a certain composition. The corresponding boiling point-composition diagram therefore shows a minimum at the same composition as in Fig. XIII.9*a* [for H_2O/pyridine system]. If a mixture with a composition at the minimum (*M*) be taken, it would boil at a fixed temperature and the vapour will have the same composition as the liquid.

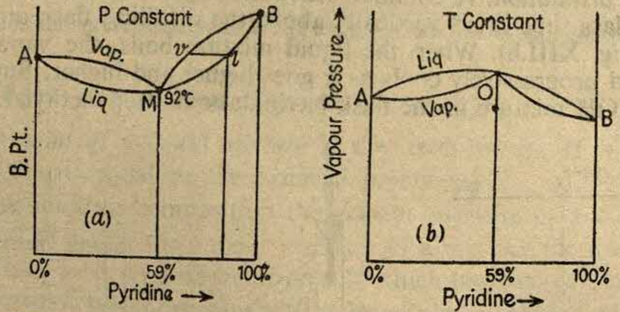


Fig. XIII.9. (*a*) B. pt.-composition diagram (*b*) Vap-pressure-composition diagram for type II system (H_2O/Pyridine).

Such a mixture which possesses a higher vapour pressure or a lower vapour pressure than any other mixture is called an **Azeotropic Mixture.** Evidently, the azeotropic mixture will have a boiling point higher or a boiling point lower than any other mixture. The azeotropic mixture distils unchanged in composition and hence these are termed *constant boiling mixtures.*

The type II water-pyridine system has a maximum vap-pressure and a minimum b. pt 92°C at a composition of 59% pyridine [Fig. XIII.9]. If we distil a water-pyridine mixture having a composition (say *l*) in which pyridine is more than 59%, the distillate will be poorer in pyridine and the residual liquid will be richer in pyridine. By repeating the process (as in type I), we can separate pure pyridine in the flask and the azeotropic mixture in the distillate. On the other hand, if a mixture containing less than 59% pyridine be distilled, the distillate will be richer in pyridine and the liquid in the flask will be richer in water. Ultimately by repetition of the process here we can obtain pure water and the azeotropic mixture. In other words, by fractional distillation, any mixture of type II can be separated only to one pure component and the azeotropic mixture. It is not possible to separate them into two pure components by distillation. If the mixture has the azeotropic composition, it will distil unchanged.

(*iii*) **Boiling pt-Composition Diagram with a Maximum.** In type III liquid pair system, the vapour pressure-composition diagram shows a minimum. Consequently, the b. pt.-composition diagram would show a maximum. That is, at a certain composition [at *M* in Fig. XIII.10*a*], there is an azeotropic mixture boiling at a fixed temperature unchanged in composition. Such a system may be illustrated with H_2O/HNO_3 mixture.

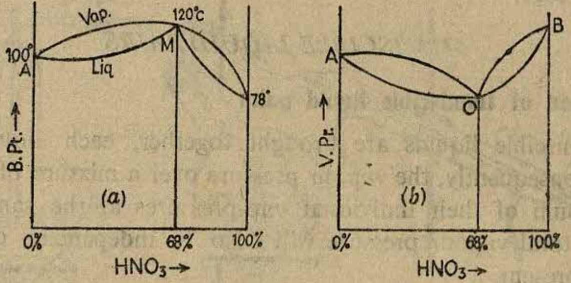


Fig. XIII.10. (*a*) B.pt.-composition diagram (*b*) Vap-pressure-composition diagram in Type III system (H_2O/HNO_3)

As in type II systems, it is easily seen that if a dilute solution of HNO_3 be distilled, it is possible to separate it into pure water and an azeotrope (68% HNO_3, b. pt. 120°C). When the azeotropic composition is reached, the liquid will distil unchanged. A higher concentration of HNO_3 cannot be obtained by distillation. On the other hand, if a conc. solution of HNO_3 be distilled, we can separate it into pure HNO_3 and the azeotropic mixture. Complete separation of HNO_3 by distillation is not possible.

Some examples of Azeotropic Mixtures:

BINARY MIXTURES TYPE II (minimum b.pt.)

Components		*Min. b. pt*	*Composition*
A	*B*	(°C)	% *of B*
H_2O	ethyl alcohol	78.1	95.6
H_2O	n-propyl alcohol	88	72
C_6H_6	acetic acid	80.05	2
H_2O	pyridine	92.6	59
CS_2	ehyl acetate	46	3

BINARY MIXTURE TYPE III (maximum b. pt.)

Components		*Max. b.pt*	*Composition*
A	*B*	(°C)	% *of B*
H_2O	HNO_3	120.5	68.0
H_2O	HCl	108.5	20.2
H_2O	HBr	126	47.5
H_2O	HI	127	57.0
H_2O	HCOOH	107	77.0
$CHCl_3$	CH_3COCH_3	64.7	20.0

The constant boiling mixture, *i.e.*, azeotropic mixture, distils unchanged. The composition of the vapour phase is the same as that of the liquid phase. The components cannot be separated by fractional distillation from the azeotropic mixture. The mixture, however, should not be regarded as a chemical compound. For, (*i*) the composition of the azeotrope rarely corresponds to stoichiometric proportions, (*ii*) the composition of the azeotrope may be altered by changing the overall pressure.

IMMISCIBLE LIQUID PAIRS

13.13. Distillation of Immiscible liquid pairs

When immiscible liquids are brought together, each liquid behaves independently. Consequently, the vapour pressure over a mixture of two immiscible liquids is the sum of their individual vap-pressures at the same temperature. Moreover, the total vapour pressure will also be independent of the quantities of each liquid present.

If P be the total pressure and p_1 and p_2 are the partial-vapour pressures of the two components, then

$$P = p_1 + p_2$$

further $$p_1 = \frac{n_1}{n_1+n_2} P \quad \text{and} \quad p_2 = \frac{n_2}{n_1+n_2} P$$

or $$p_1/p_2 = n_1/n_2$$

where n_1 and n_2 are gm-moles of the two components in the vapour phase, in any given volume. At the given temp., the vap-pressures of the two components are fixed, p_1/p_2 is constant, so n_1/n_2 is also fixed. That is, the vapour-composition is always the same, as long as both liquids are present. If weights of the components in the vapour-phase (*i.e.*, the distillate) be w_1 and w_2, then

$$\frac{p_1}{p_2} = \frac{w_1/M_1}{w_2/M_2}, \qquad (M_1, M_2 \text{ are mol. wts})$$

or $$\frac{w_1}{w_2} = \frac{p_1 M_1}{p_2 M_2} \qquad \ldots (\text{XIII.7})$$

The weights of two components in the distillate depend on the mol. wts and vapour pressures of the two pure components. We shall presently see that this relation is taken advantage of in steam distillation.

As the temperature is raised, the vapour pressure of each liquid will increase, so that total vapour pressure will rise. When this total vapour pressure is equal to the external pressure, the mixture will boil and distillation goes on with a constant composition of the distillate. The boiling point will be lower than the boiling point of either of the two liquids.

Steam distillation. When a liquid (or a solid) X, which is immiscible with water is to be separated from other non-volatile impurities, it is often distilled with steam. The process becomes particularly useful when the substance X is high-boiling and decomposes near its normal boiling point. In steam distillation, the substance is distilled with steam at a temperature considerably below (near about 100°C) its normal boiling point and the danger of decomposition is avoided. To illustrate: iodobenzene (b. pt. 188°C) is purified by steam distillation at about 98°C. At this temperature, $p_{H_2O} = 712$ mm and $p_{\text{iodobenzene}} = 48$ mm, so that total pressure = 760 mm.

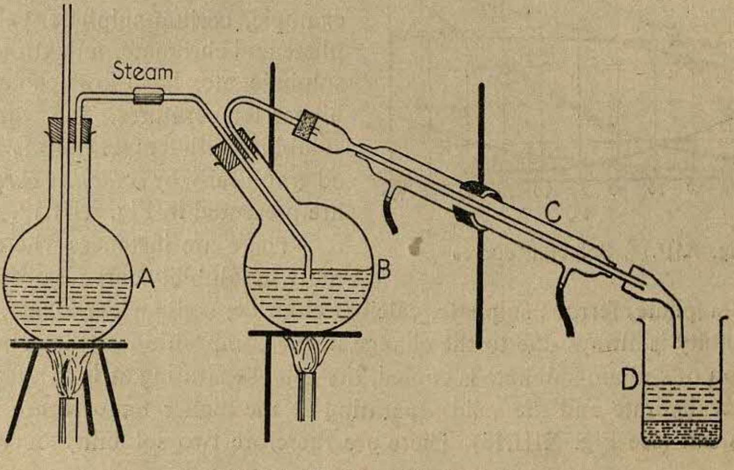


Fig. XII.11. Steam distillatior

The liquid to be purified is taken in a flask mixed with water and heated, Steam from a separate generator is also simultaneously injected. When the temperature is raised high enough to make $p_1 + p_2 = 760$ mm, the mixture distils with a composition given by equation XIII.7.

In the case of iodobenzene mentioned above.

$$\frac{w_1}{w_2} = \frac{M_1 p_1}{M_2 p_2} = \frac{204 \times 48}{18 \times 712} \approx \frac{7}{9} \text{ (approx.)}$$

Hence, out of every 16 gms of distillate, 7 gms would be iodobenzene. Though the vap-pressure of iodobenzene is much lower, but its high molecular weight counterbalances so as to make the relative yield appreciably large.

IV. SOLUTION OF SOLIDS IN LIQUIDS

13.14. Solubility

The solubility of a solid in a liquid is defined as the number of grams of solid (solute) which can be dissolved in 100 *grams of liquid (solvent) at a given temperature* *in presence of excess of the solid.* The solubility depends upon the nature of the solid and the liquid and especially on temperature. Thus, sulphur is soluble in alcohol but not in water. The solubility of nitre in water is 86 at 50°C and 247 at 100°C. From the definition given above, *a saturated solution is one whose composition does not change at a given temperature even in the presence of excess solute.*

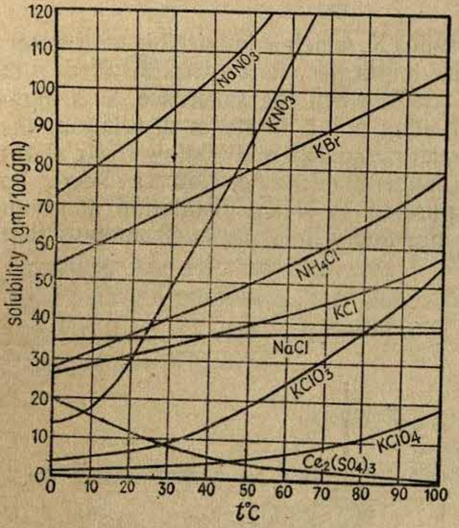


Fig. XIII.12. Solubility curves

Every solid is soluble in a given liquid, when the solubility is extremely small, we regard it as *insoluble*. Thus, AgI is insoluble in water, but really it dissolves to an extent of 10^{-8} gm ions of silver per litre.

Mostly the solubility of solids in liquids increases with rising temperature. There are some exceptions; for example, cerium sulphate, calcium sulphate and chromate, anhydrous sodium sulphate etc. have lower solubilities at higher temperatures. The variation of solubility with temperature is represented graphically by *solubility curves.* A few are presented in Fig. XIII.12.

There are instances where discontinuity in solubility curve is observed, e.g., sodium sulphate, ferrous sulphate, calcium chloride, sodium carbonate, etc. This discontinuity is always due to the change in the composition of the solute salt. If a solution of sodium sulphate is cooled, the solid separating at lower temperature is the decahydrate and the solid separating at the higher temperature is the anhydrous salt (see Fig. XIII.13). There are therefore two solubility curves of two solutes. In ferric chloride, calcium chloride and other solutions there occur more than one discontinuity or break in the solubility curves. At the breaking point, one hydrate passes to another hydrate or to the anhydrous salt. Every system has its fixed break, called the transition point.

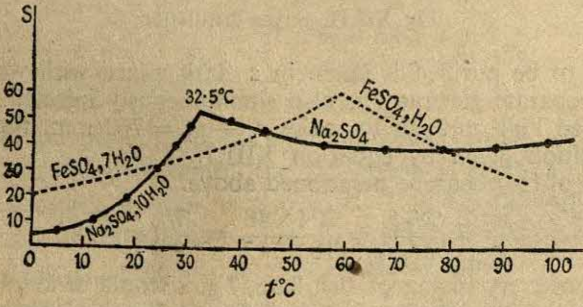


Fig. XIII.13. Discontinuities in solubility curves

Most of the solids dissolve with absorption of heat and hence the process is endothermic. According to Le-Chatelier's principle, the endothermic dissolution should increase with temperature-rise. The common solubility curves confirm this. The cases where solubility decreases with rise in temperature, there would be heat evolution. The quantitative relation of solubilities S_1 and S_2 at temperatures T_1° and T_2°K is given by the reaction isochore, as

$$\log\frac{S_1}{S_2} = \frac{\triangle H_s}{2.303R}\left[\frac{1}{T_2} - \frac{1}{T_1}\right]$$

where $\triangle H_s$ is the molar heat of solution.

The mechanism of dissolution of a solid in a liquid may be different in different cases. When an ionic crystal (say NaCl) in dissolved in a polar liquid (say H_2O), the negative ends of the H_2O molecule are drawn towards the positive Na^+ ions on the crystal surface. The positive ends of the H_2O molecules approach the negative Cl^- ions. When the attractive force between the opposite charges of the solute and solvent exceeds the electrical forces between the ions in the crystal, the ions are pulled out into the solution. And these ions are always surrounded by solvent molecules, *i.e.*, the ions are solvated which prevents them from coming together and aggregating. On the other hand, when non-ionic solids like urea, sugar etc. are placed in water, hydrogen-bonding occurs between the water and solute molecules and this leads to dissolution.

The dissolution of the solid involves two distinct-processes, (*i*) work is done against the electrostatic forces existing between the particles in the crystal (*ii*) the dissolved particles remain associated with or sometimes united with some solvent molecules. From the thermodynamic point of view, in the process of dissolution two oppositive phenomena are involved. The absorbed heat of dissolution leads to an enthalpy-increase for the dissolved state. Hence, the process of dissolution is opposed by it. But the dissolution would lead to a large increase in randomness and hence in large rise in entropy. This randomness favours dissolution. Whenever $T\triangle S$ is larger than the enthalpy-rise, free energy decreases and dissolution occurs.

V. SOLUTION OF SOLIDS IN SOLIDS

13.15. Solid Solutions

It is sometimes observed that two substances on being melted together form a homogeneous liquid and the melt, on cooling, deposits a solid which is a homogeneous mixture of both the components. This is the solid solution. This phenomenon is observed often in alloys and in mixed crystals of isomorphous compounds. Examples: Au-Pt, Cu-Ni, Co-Ni, Ag-Pd, AgCl-NaCl, $PbBr_2$-$PbCl_2$, KCNS-NH_4CNS, naphthalene—β-naphthol, etc.

A solid solution does not melt at a fixed point but over a certain range of temperature, the liquid and solid compositions therefore vary. Only when the solid melts completely, its composition becomes the same as that of the initial solid. The temperature at which solid begins to be deposited from the melt is called the *freezing point* of the mixed solution. The temperature at which the liquefaction of a solid solution just begins is called its melting point. The plot of freezing points against composition of the liquid is called the *liquidus*. The plot of melting points of the solid solution against composition of the solid is called the *solidus* (see

Fig. XIII. 14). The liquidus is above the solidus. Let us take the system of gold-platinum alloy as an example.

The system Au-Pt. In the system Au-Pt, the two components are completely miscible in the liquid as well as in the solid phases at all compositions. The behaviour of the system can be followed from the diagram given in Fig. XIII.14.

The freezing point of pure gold is 1062°C and that of pure platinum 1755°C. The addition of Pt to Au raises the m.pt. whereas the addition of Au to Pt lowers the m.pt. The freezing pts. of all mixtures lie between the f.pts of Au and Pt. This is also true of the m.pts of all solid solutions. The upper curve in the diagram represents the liquidus and the lower curve the solidus. Thus the components form a continuous series of solid solutions with no maximum or minimum point of convergence of the two curves. It is easily understood that a liquid solution of composition, say x, is in equilibrium with a solid solution of composition x'. This happens at every temperature between the limits 1062° and 1755°C. Above the liquidus the system is entirely liquid and below the solidus the system is entirely solid. In the region in between the solidus and liquidus the system would be partly liquid and partly solid. If the system be kept in a state represented by z, then it would be a mixture of liquid phase of composition x and solid phase x' in equilibrium.

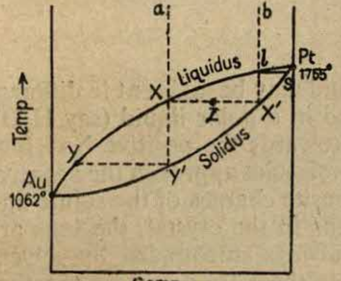


Fig. XIII.14 Phase-diagram of the system Pt-Au

If a Au-Pt melt of composition '*a*' be slowly cooled, the first solid, which will indeed be a solid solution, will separate when the point x is reached. The composition of the solid separating out will be x', *i.e.*, richer in platinum. In consequence, the residual liquid phase will be richer in gold. The general principle is that *the concentration of the component by the addition of which freezing point is raised is greater in the solid than in the liquid phase.* On further cooling below x, more and more solid solution will separate out and the residual liquid in equilibrium will be deprived more and more of its platinum. The composition of the liquid solution will move along xy while that of the solid solution along $x'y'$. At y' vertically below x, the system entirely solidifies and just at the moment of complete solidification, the liquid composition is y and solid composition y'.

Such behaviour also explains the **fractional crystallisation** of the components. The solid separating at x', if removed, melted and again cooled, solid solution will separate out at l and will have the composition s, in which Pt-content will be much higher. The process could be repeated with the solid s, until the component Pt is reached. On the other hand, by taking the liquid fractions at y, a successive repetition would enable us to obtain liquid fractions with higher and higher percentage of gold and ultimately pure gold would separate out. Both the components are thus available in pure forms from such a system by fractional crystallisation.

EXERCISES

1. (*a*) Express the relation between molar concentration and mol-fraction of a very dilute solution of sugar in water. (*b*) A sample of spirit contains 92% ethanol by weight and rest water, what is the mole-fraction of alcohol?

2. State and explain Henry's Law in its different forms. What is meant by absorption coefficient? What are the limitations of Henry's Law?

3. Discuss the influence of temperature and pressure on the solubility of gases in liquids. "With rise in temperature, the solubility of a gas in a liquid decreases but the solubility of a solid in most cases increases." Explain.

4. State what are likely to happen when the following are boiled: (*a*) water containing dissolved air (*b*) dil KCl solution (*c*) dil HCl solution.

5. Suggest examples of three differently behaving partially miscible liquid pairs. Describe the behaviour of water-phenol system, clearly defining its critical solution temperature.

6. State Raoult's Law. What are its limitations? How would you define an ideal solution? Would Henry's Law follow Raoult's Law in ideal systems?

7. Prove that in an ideal binary miscible liquid pair, the vapour contains more of the component having lower normal boiling point.

8. Discuss the variation of vapour pressure of a zeotropic mixture with composition. Explain with temp-composition diagram the separation of its components by fractional distillation.

9. What are azeotropic binary liquid systems? Discuss the distillation of the two types of such azeotropic systems.

10. Write explanatory notes on: (*i*) consulate temperature, (*ii*) partial pressure, (*iii*) Zeotropic mixtures, (*iv*) steam distillation, (*v*) solid solution.

11. Explain the principle involved in the process of steam distillation.

At a pressure of 1 atm. a mixture of water and nitrobenzene boils at 99°C. The vap-pressure of water at 99°C is 733 mm. Estimate the proportion of water and nitrobenzene in the distillate. [Ans. H_2O: nitrobenzene = 4:1]

12. A mixture of chlorobenzene and water boils at 90.3°C under a pressure of 740.2 mm. The vap-pressure of water at this temp. is 530.1 mm. What is the proportion of the two liquids, by weight, in the distillate. (Kurukshetra Univ.) [Ans. 2.5 : 1.0 approx]

13. Nitrobenzene can be distilled with steam under 1 atm pressure at 99.2°C. Calculate the amount of steam necessary to distil 100 gm nitrobenzene. The vap-pressure of water at 99.2°C is 739 mm. (Delhi Univ.) [Ans. 513 gm]

14. Discuss the principle of fractional distillation of miscible liquid pairs [Cal. Univ., Lucknow Univ., Kerala Univ.]

15. Discuss the separation of the following in the light of the theory of fractional distillation: (*i*) methyl alcohol from its aqueous solution, (*ii*) Ethyl alcohol from its aqueous solution.

16. Water and propyl alcohol (b.p. 97.2°C) form an azeotropic mixture (b.p. 87.7°C) with 71.7% propyl alcohol. Which component can be obtained pure by fractional distillation of a mixture containing 50% by weight each.

17. Benzene and Toluene form an ideal solution. At 50°C. their vapour pressures are $p_{C_6H_6} = 270$; $p_{C_7H_8} = 92$ mm. What is the vapour pressure over the solution at 50°C if a solution is prepared from 39.0 gm benzene and 23.0 gm toluene? [Ans. 210.6 mm]

18. Critically examine the following statements: (*a*) An azeotropic mixture can be considered as a chemical compound since it vaporises unchanged in composition. (*b*) With rise in temperature, the ratio of the partial pressure of a component and total vapour pressure would increase. (*c*) Pure nitric acid can be obtained by distillation of dil. nitric acid solutions. (*d*) The solubility of solids in liquids always increases smoothly with rise in temperature.

lowering of vapour-pressure due to the different solutes in any solvent was found to be nearly the same (Table).

TABLE : $\Delta p/p_1^\circ$ IN DIFFERENT SOLVENTS (RAOULT)

Solvent→	H_2O	CS_2	$CHCl_3$	C_6H_6	CCl_4
$\Delta p/p_1^\circ$→	0.0102	0.0105	0.0105	0.0106	0.0105

14.2. Measurement of Vapour Pressure Lowering

Of the several methods employed for the determination of vapour pressure lowering, only a few are briefly described here.

(*i*) **Isoteniscope method** (Smith & Menzies). A sketch of the apparatus is given in Fig. XIV.2. A bulb A is half-filled with the liquid under investigation. This bulb is fused to a U-tube B containing a few c.c. of the same liquid. This is connected to a condenser, a manometer and finally to a pump in series. The liquid in bulb A is boiled to drive out the air completely and then the system is placed in a thermostat T. The pressure above the liquid in A is the vapour pressure of the liquid at that temperature. Then air is slowly introduced until the levels of the liquid in two limbs of the U-tube become equal. The reading in the manometer is noted and subtracting it from the Barometric reading at that time, the vapour pressure of the liquid is obtained. The experiment is to be repeated next with the solution, so that both p_1° and p_1 are obtained.

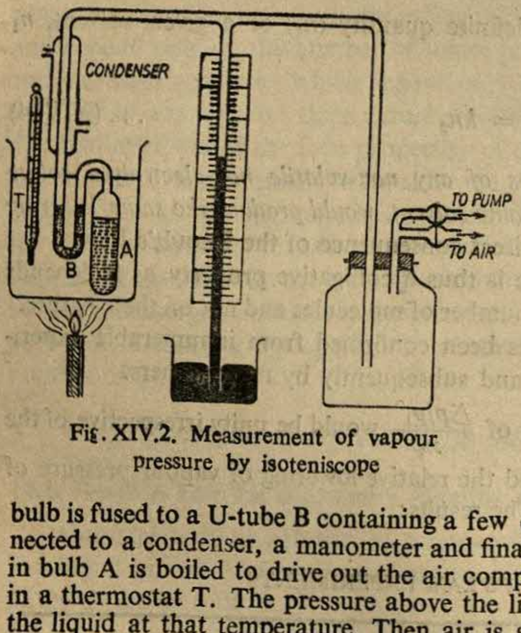


Fig. XIV.2. Measurement of vapour pressure by isoteniscope

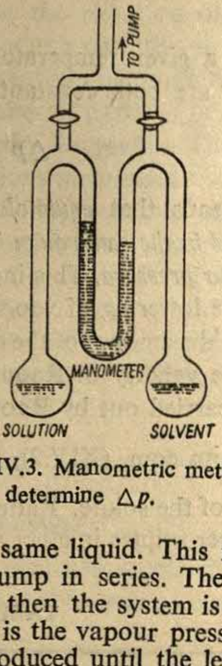


Fig. XIV.3. Manometric method to determine Δp.

(*ii*) **Differential Manometric Method:** The apparatus required in this method is shown in Fig. XIV.3. Two bulbs, one containing the pure solvent and the other the solution, are interconnected through a U-Tube serving as a differential manometer. The manometric liquid generally used is *n*-butyl phthalate which is light and has low volatility. The bulbs are also connected to a pump. The air is completely removed by the pump first and then it is kept in a thermostat. When equilibrium is established, there would be a difference in the levels of liquid in the U-tube which gives directly the difference of vapour pressures of solvent and solution, $(\Delta p = p_1^\circ - p_1)$.

But the more commonly used method is that of Ostwald and Walker, in which the relative lowering of vapour pressure can be directly obtained.

(*iii*) **Ostwald-Walker's Dynamic method:** A steam of dry air is slowly passed through a previously weighed series of bulbs containing the solution (Fig XIV.4). The air takes up vapour from the solution until it is saturated up to pressure p_1, which is the vapour-pressure of the solution at that temperature. The actual loss of vapour from the bulbs is obtained by subsequently weighing the bulbs. The loss of weight w_1 is proportional to p_1, *i.e.*, $w_1 = kp_1$.

The air (already saturated with vapour up to pressure p_1) is next passed through another series of bulbs, also previously weighed and containing pure solvent.

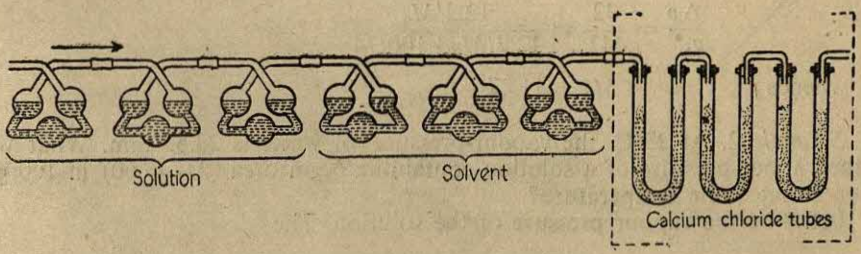


Fig. XIV.4 Ostwald-Walker method for measuring vap-pressure lowring

Since the vapour pressure of pure solvent p_1° is greater than p_1, the air will take up some more vapour from pure solvent until the air is saturated to pressure p_1°. The bulbs are weighed again to obtain the loss of weight, w_2, which is required to saturate the air from pressure p_1 to p_1°.

$$\therefore\ w_2 \text{ is proportional to } (p_1^\circ - p_1),\ i.e.,\ w_2 = k(p_1^\circ - p_1)$$

Finally the air is passed through a weighed series of U-tupes containing an absorbent for the vapour of the solvent, *e.g.*, anhydrous $CaCl_2$ if the solvent is water. The increase in weight of the U-tubes is determined, which gives $w_1 + w_2$. This weight is the measure of the vapour required to saturate the air up to pressure p_1°.

Hence $$\frac{p_1^\circ - p_1}{p_1^\circ} = \frac{w_2/k}{(w_1+w_2)/k} = \frac{w_2}{w_1+w_2}$$

Since the quantities on the right-hand side are known the relative lowering of vapour-pressure is obtained. The temperature must be kept constant throughout.

14.3. Determination of Molecular Weights

The molecular weight of a dissolved non-volatile non-electrolyte solute can be determined with the help of Raoult's Law. Consider a solution containing w_2 gm solute (mol. wt. M_2) in w_1 gm solvent (mol. wt. M_1). Then the moles of solute $n_1 = w_2/M_2$ and moles of solvent. $n_1 = w_1/M_1$. Now, from equation (XIV. 2),

$$\frac{\triangle p}{p_1^\circ} = \frac{n_2}{n_1+n_2} = \frac{w_2/M_2}{w_2/M_2 + w_1/M_1} \qquad \text{. . . (XIV. 5)}$$

In dilute solutions, $n_1 \gg n_2$, hence

$$\frac{\triangle p}{p_1^\circ} = \frac{n_2}{n_1} = \frac{w_2/M_2}{w_1/M_1} = \frac{w_2 M_1}{w_1 M_2} \qquad \text{. . . (XIV.6)}$$

The relative lowering of vapour pressure ($\triangle p/p_1^\circ$) is experimentally measured. The use of equations (XIV.5, 6) would enable the evaluation of the molecular weight of the solute. The molecular weight M_1 of the solvent is assumed to be known.

Example 1. At 20°C, the vapour pressure of ether dropped from 442 mm to 410 mm when 12.2 gm of a solute was dissolved in 100 gm ether ($M_1 = 74$). Calculate the mol. wt. of the solute.

$p_1^\circ = 442$ mm. $\triangle p = 442-410 = 32$ mm. $n_1 = 100/74$, $n_2 = 12.2/M_2$

$$\therefore \qquad \frac{\triangle p}{p_1^\circ} = \frac{32}{442} = \frac{12.2/M_2}{12.2/M_2+100/74}$$

whence $$M_2 = 115.7$$

Example 2. At 25°C, the vapour-pressure of water is 23.55 mm. What will be the vapour-pressure of a solution containing 6 gm urea ($M_2 = 60$) in 100 gm water at the same temperature?

Let P be the vapour pressure of the solution. The

$$\frac{P_0-P}{P_0} = \frac{n_2}{n_2+n_1}$$

or $$\frac{23.55-P}{23.55} = \frac{6/60}{6/60+100/18} = \frac{0.1}{0.1+5.55}$$

whence $$P = 23.13 \text{ mm.}$$

Example 3. A current of dry air is passed through a series of bulbs containing a solution of 8.914 gm of nitrobenzene in 100 gm of alcohol and then through a series of bulbs containing pure alcohol, at the same temperature. After the passage of air, the loss in weight of bulbs containing the solution was 2.034 gm and that of the bulbs of pure alcohol was 0.0685 gm. Calculate the mol-weight of nitrobenzene.

Let P and P_0 be the vapour pressures of alcohol over the solution and the pure solvent at that temperature. The solute is regarded as non-volatile.

On passing through the solutions, the air was saturated up to the pressure P, by vaporising 2.034 gm of alcohol. Subsequently, the air was led through pure solvent and it was saturated to pressure P_0, for which it absorbed a further quantity of alcohol vapour, *i.e.*, 0.0685 gm. Hence the total amount of vapour required to saturate the same volume of air up to pressure $P_0 = 2.034 + 0.0685 = 2.1025$ gm.

Obviously, $P \propto 2.034$; and $P_0 \propto 2.1025$

Hence $$\frac{P_0-P}{P_0} = \frac{0.0685}{2.1025}$$

But $$\frac{P_0-P}{P_0} = \frac{n_2}{n_1} = \frac{\dfrac{8.914}{M_2}}{\dfrac{100}{46}} = \frac{8.914\times 46}{100\times M_2}; \text{ (mol. wt. of alcohol = 46)}$$

or $$\frac{0.0685}{2.1025} = \frac{8.914\times 46}{100\times M_2}$$

whence, $$M_2 = 125.8$$

B. ELEVATION OF BOILING POINT OF SOLUTIONS

14.4. Laws of Elevation of Boiling Point of Solutions

The vapour pressure of a pure solvent increases with rise in temperature. This is shown by AB in Fig. XIV.5. When a non-volatile solute is dissolved in the solvent, the vap-pressure of the solution will be lower than that of the pure solvent at any given temperature. Here also the vapour pressure of the solution increases with rise in temperature as shown by CD in the figure.

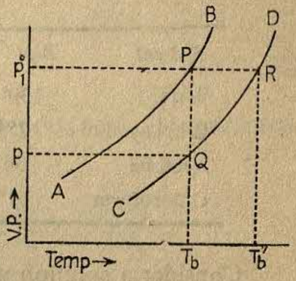


Fig. XIV.5 Elevation of b.pt. of a solution

A liquid boils when its vapour-pressure becomes equal to that of the superincumbent pressure. Let T_b be the boiling temperature of the pure solvent and so its vapour pressure equals one atmosphere p_1° at this temperature. But at this temperature the solution will have a vapour pressure (p) lower than one atmosphere and hence it will not boil. With further increase in temperature, say to T_b', the vapour-pressure over the solution rises to one atmosphere when the solution would boil. This means that *the solution has a higher boiling point than that of the pure solvent.* The increase in boiling temperature is given by PR $= T_b' - T_b = \triangle T_b$, and change in pressure is given by PQ $= p_1^0 - p = \triangle p$. As the solutions are dilute $\triangle T_b$ and $\triangle p$ are small quantities.

Extensive investigations on the boiling point elevation with innumerable solutions carried out by Raoult, Beckmann and others led to two generalisations or empirical Laws, often called the *Raoult's Laws of the elevation of boiling point of solutions.*

Law 1. *The elevation of boiling point ($\triangle T_b$) of a solution is proportional to the molality or molal concentration (m) of the solution.*

That is, $\triangle T_b \propto m$; or $\triangle T_b = k_b . m$ ... (XIV.7)

where k_b is a constant, called *molal elevation constant or ebullioscopic constant.* The elevation of b.pt. depends on the molality and not on the nature of the solute. Hence it is a colligative property.

Law 2. *Equimolecular amounts of different substances dissolved in the same amount of a given solvent increase the boiling point to the same extent.*

If solutions of the same concentration (m) be taken in different solvents, $\triangle T_b$ would be different. It means that k_b has different values for different solvents.

These laws are strictly valid for *dilute* solutions of non-volatile non-electrolytes.

For a solution, where $m=1$, $\triangle T_b = k_b$, *i.e.*, k_b is equivalent to the elevation of boiling temperature for a solution of unit molality *i.e.* one mole solute dissolved in 1000 gm solvent. Hence k_b is called *molal elevation constant* or *ebullioscopic constant.* In fact, one molal solution would be too concentrated to obey

Raoult's Law and equation XIV. 7. The magnitude of k_b is to be evaluated by measuring $\triangle T$ for a dilute solution of known m using the relation. The molal elevation constant for different solvents would vary; the values of some of these are given in the Table below:

TABLE: MOLAL EBULLIOSCOPIC CONSTANTS

Solvent	*B.pt* (°C)	K_b	*Solvent*	*B.pt.*(°C)	K_b
Water	100°	0.513	Carbon tetrachloride	78.8°	5.02
Ethyl alcohol	75.4°	1.2	Benzene	80°	2.6
Acetone	56°	1.7	Acetic acid	118	3.12
Chloroform	61°	3.85	Ethyl ether	34.5°	2.16

Consider a solution where w_2 gm solute are dissolved in w_1 gm solvent. The mol. wt. of the solute is M_2. Hence

moles of solute dissolved $= w_2/M_2$,

Or, w_1 gm solvent contains w_2/M_2 moles solute

i.e. 1000 gm solvent contains $\frac{w_2 \times 1000}{M_2 \times w_1}$ moles solute.

Hence, molality of the solution, $m = \frac{w_2 \times 1000}{M_2 \times w_1}$ ...(XIV.8)

The equation (XIV. 7) would then be,

$$\triangle T_b = k_b . \frac{w_2 \times 1000}{M_2 \times w_1} \quad \text{...(XIV.9)}$$

14.5. Thermodynamic Derivation of the Laws of Boiling Point-Elevation

In the solution vapour-pressure curve CD (Fig. XIV.5) at the point Q, the pressure is p_1 and temperature is T_b. At the point R, the pressure is $p_1{}^0$ and temperature is T_b'. Applying Clausius-Clapeyron equation at these points, we have

$$ln\ p_1 = -\frac{L_v}{RT_b} + Z\,(\text{constant})\,; \qquad ln\ p_1{}^0 = -\frac{L_v}{RT_b'} + Z\,(\text{constant})$$

i.e.,
$$ln\frac{p_1}{p_1{}^0} = -\frac{L_v}{R}\left[\frac{1}{T_b} - \frac{1}{T_b'}\right] = -\frac{L_v}{R} \cdot \frac{T_b' - T_b}{T_b T_b'}$$

where L_v is the molar latent heat of vaporisation. Hence,

$$ln\left(1 - \frac{p_1{}^0 - p_1}{p_1{}^0}\right) = -\frac{L_v}{R} \cdot \frac{\triangle T_b}{T_b{}^2}, \ (T_b \text{ is very close to } T_b', \text{ hence } T_b T_b' \approx T_b{}^2)$$

or,
$$ln\left(1 - \frac{\triangle p}{p_1{}^0}\right) = -\frac{L_v}{R} \cdot \frac{\triangle T_b}{T_b{}^2}$$

where $\triangle T_b$ = elevation of the boiling point.

Since $\frac{\Delta p}{p_1^0}$ is quite small, expanding and neglecting higher powers,

$$-\frac{\Delta p}{p_1^0} = -\frac{L_v}{R}\cdot\frac{\Delta T_b}{T_b^2}; \quad \text{or} \quad x_2 = \frac{L_v \Delta T_b}{RT_b^2},$$

since from Raoult's Law, $\frac{\Delta p}{p_1^0} = x_2$ (mol-fraction of the solute).

$$\therefore \qquad \Delta T_b = \frac{RT_b^2}{L_v}\cdot x_2 \qquad \ldots\text{(XIV.10)}$$

This is the relation between the elevation of the boiling point with the concentration of the solute in the solution.

In dilute solutions, mol-fraction, $x_2 = \frac{n_2}{n_1+n_2} \approx \frac{n_2}{n_1} = \frac{w_2/M_2}{w_1/M_1}$.

Hence, $$\Delta T_b = \frac{RT_b^2}{L_v}\cdot\frac{w_2 M_1}{w_1 M_2}$$

when w_2 gm of solute are dissolved in w_1 gm of solvent; M_2 and M_1 are the molecular weights of solute and solvent respectively.

Then $\Delta T_b = \frac{RT_b^2}{L_v/M_1}\cdot\frac{w_2}{w_1 M_2} = \frac{RT_b^2}{l_v}\cdot\frac{w_2}{w_1 M_2}$, ($l_v$ = latent heat per gm)

$$\text{or} \qquad \Delta T_b = \frac{RT_b^2}{1000 \times l_v}\cdot\left[\frac{w_2 \times 1000}{w_1 \times M_2}\right] = \frac{RT_b^2}{1000 \times l_v}\cdot m, \qquad \text{(XIV.11)}$$

since quantity within the paranthesis is the molality (m) of the solution. For a given solvent l_v and T_b are constant, we may write

$$k_b = \frac{RT_b^2}{1000 \times l_v} \qquad \ldots\text{(XIV.12)}$$

and hence $$\Delta T_b = k_b . m \qquad \ldots\text{(XIV.13)}$$

The constant k_b has a definite value for each solvent.

The empirical laws presiously mentioned are thus rigidly established.

14.6. Measurement of Elevation of Boiling Point

In measuring the boiling point elevation of a solution, sufficient precaution is needed to avoid superheating and any loss of solvent. Different methods are employed to measure ΔT_b.

(a) **Beckmann's Method.** An arrangement as in Fig. XIV.6 is used. A wide glass test tube *A* with a side-arm *B* connected to a condenser is taken. A weighed amount of pure solvent is taken in *A* which is fitted with a special thermometer called Beckmann thermometer. The tube *A* has a Pt-wire sealed at the bottom and has some glass beads inside. These are necessary to prevent superheating. The liquid in *A* is then slowly heated until it boils uniformly and steadily; the vapour produced is condensed in the condenser and returns to the liquid so that the amount (or conc.) remains unaltered. The tube *A* is not heated directly but is surrounded by a circular double-walled vessel containing pure solvent which is also kept boiling. The whole thing is heated on an asbestos box, the latter being provided with chimneys *H* for circulation of air. The boiling tube is placed on asbestos rings. All these precautions are meant for eliminating super-heating.

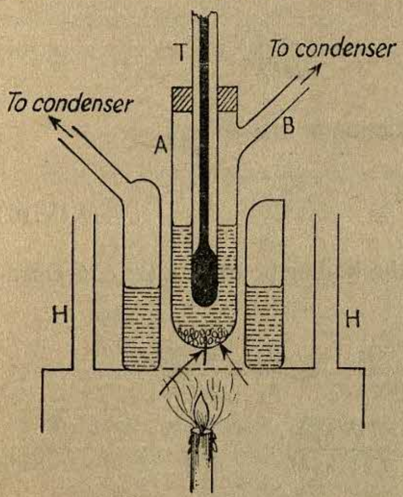


Fig. XIV.6. Beckmann's boiling pt. apparatus

After the boiling point of the pure solvent is recorded in the thermometer, a small amount of the solute (of known weight) is added through the side tube to the liquid. The boiling temperature is then again noted in the same thermometer. The difference of the two readings in the Beckmann thermometer gives the elevation in boiling temperature.

The Beckmann thermometer is specially designed to obtain difference of temperature; it does not record the actual boiling pt. of either the solvent or the solution. It consists of a large bulb leading to a long capillary tube (Fig. XIV.7) connected with another bulb serving as reservoir for excess mercury at the top. Since the bulb is large and the capillary fine, a small temperature change makes a considerable movement of the mercury level in the capillary tube. Temperature differences about the hundredth part of a degree can thus be recorded. The scale of the Beckmann thermometer has only 6°, divided into 600 divisions. To keep the mercury head within the scale at different temperatures, it is essential to vary the amount of mercury in the lower bulb. When the boiling points are relatively low, more mercury is transferred to the bottom bulb. But when boiling temperatures are higher, mercury is transferred from the bottom to the top reservoir by heating and detatching from the capillary thread. For details of setting such a thermometer, Findlay's Practical Physical Chemistry may be consulted.

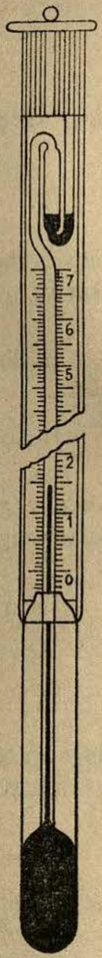


Fig. XIV.7 Beckmann thermometer

(b) **Cottrell's Method.** In Fig. XIV.8 is given a sketch of the Cottrell's apparatus. A wide glass tube '*A*' is taken containing a known amount of liquid. A sensitive thermometer, which also serves as its stopper, is inserted in the tube such that the bulb of the thermometer is at some distance above the liquid surface. The tube is also provided with a side-tube connected to a condenser so as to receive back the vapour cooled and condensed. Inside the tube there is an inverted funnel shaped tube (*B*) over a piece of porous disc. The bifurcated stem of the funnel ends just near the thermometer bulb. The liquid is heated with a small flame from below. When a steady state of boiling is reached, the vapour along with a stream of boiling liquid bubbles up the stem of the funnel and is discharged on the bulb of the thermometer. The temperature recorded then is the precise boiling temperature of the liquid. Weighed pellets of solute are then added and the boiling points of solutions are measured as before. The increase in boiling temperatures due to addition of solute is thus known.

(c) **Landsberger's method.** A sketch of the apparatus used in this method is given in Fig. XIV.9. Pure solvent is taken in the flask A and is heated. The solvent-vapour enters into a graduated boiling tube B. The middle portion of the boiling tube is blown into a bulb with a hole C. A sensitive thermometer T is fitted into the boiling tube. This boiling tube which contains intially about 10 c.c. solvent is surrounded by a jacket through which the hot vapour escaping from the hole passes. On passing the vapour, the temperature inside the boiling tube rises and the solvent in it steadily boils. The temperature is recorded. The operation is stopped for a few minutes and a known quantity of solute (0.4 gm approx.) is introduced. The boiling point is redetermined. The difference of the two readings gives $\triangle T_b$. The volume of the solution is then read from the scale after first removing the delivery tube and the thermometer. The mass of the solvent is calculated by multiplying their volume with its density at the boiling temperature.

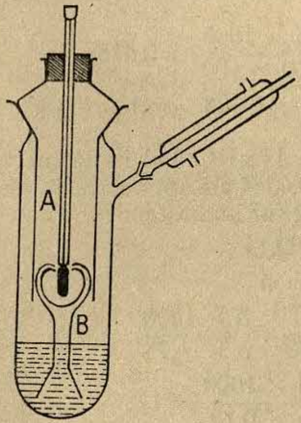


Fig. XIV.8. Cottrell's apparatus

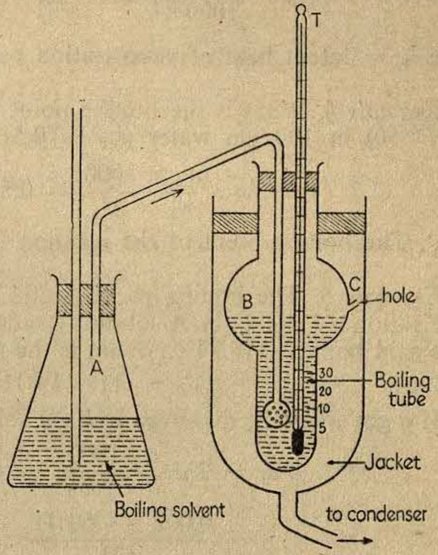


Fig. XIV.9. Landsberger apparatus

14.7. Determination of Molecular Weights from B. Pt. Elevation

From eqn. (XIV.12), $\triangle T_b = k_b . m$

Since molality, $m = w_2 \times 1000/(w_1 \times M_2)$; (eqn XIV. 8)

$$\therefore \quad \triangle T_b = k_b \times \frac{w_2 \times 1000}{w_1 \times M_2}$$

$$\text{or} \quad M_2 = k_b \times \frac{w_2 \times 1000}{\triangle T_b \times w_1} \qquad \text{. . . (XIV.14)}$$

Thus, a measurement of the elevation of boiling point ($\triangle T_b$) would enable us to determine the mol. wt. (M_2) of the solute. The value of k_b can be experimentally found out from the same equation using a solute of known mol. wt. It is also possible to compute k_b from equation (XIV.12).

$$k_b = \frac{RT_b^2}{1000 \times l_v} = \frac{0{\cdot}002T_b^2}{l_v} \quad ((\text{since } R \approx 2\text{ cal})$$

where l_v = latent heat of vaporisation per gm of solvent.

Example 4. What is the boiling point of a solution containing 5.00 gm urea (M_2 = 60) in 100 gm water (k_b = 0.513)?

$$\triangle T_b = k_b \, . \, \frac{w_2 \times 1000}{w_1 \times M_2} = 0.513 \times \frac{5 \times 1000}{60 \times 100} = 0.428°$$

$\therefore$ The boiling point of the solution = 100° + 0.428° = 100.428°C

Example 5. The boiling pt. of acetic acid is 118.1°C and its latent heat of vaporisation is 121 cal/gm. A solution containing 0.4344 gm anthracene in 44.16 gm acetic acid boils at 118.24°C. What is the mol. wt. of anthracene?

Now $\triangle T_b = 118.24 - 118.1 = 0.14°$

If a gm solute be dissolved in b gm solvent, then

$$M_2 = K_b . \frac{a \times 1000}{b \times \triangle T_b} = \frac{RT_b^2}{l \times 1000} \cdot \frac{a \times 1000}{b \times \triangle T_b}$$

$$= \frac{0.002 \times (391.1)^2}{121} \cdot \frac{0.4344 \times 1000}{44.16 \times 0.14} = 178$$

C. DEPRESSION OF FREEZING POINT OF SOLUTIONS

14.8. Lowering of Freezing Point of solutions

The freezing point of a liquid is the temperature at which the liquid and the solid phases have the same vapour pressure, so that they continue to exist in equilibrium. In fig. XIV.10, AB and AC are the vapour pressure curves of liquid and solid phases of pure solvent. These interesect at A which indicates the freezing temperature T_f of pure solvent, the vapour pressure at A being p_1^0.

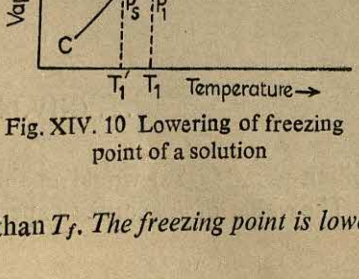


Fig. XIV. 10 Lowering of freezing point of a solution

The vapour-pressure curve of the solution of a non-volatile solute will be lower than that of the pure solvent and is represented by DE. At the temperature T_f, the vapour pressure of the solution is p_1 (say) at the point R; and this pressure is less than that of the solid which is p_1^0. Hence if solid is added to this solution, the former will melt to attain equilibrium. The solution on being cooled further, its vapour-pressure curve will meet the curve AC at the point Q, where (at pressure say p_s, and temperature T_f') the solution will have the same vapour pressure as the pure solid. Hence T_f' is the freezing point of the solution and T_f' is lower than T_f. *The freezing point is lowered due to the presence of the solute.* It is necessary to emphasise here that the solid phase at Q must be that of the pure solvent and should not be a solid solution or a compound.

Raoult and others measured the depression of the freezing point of various solutions. The results of these experiments led to the formulation of two empirical laws.

Law I. *The depression of the freezing point* ($\triangle T_f$) *of a solvent due to the presence of a solute is proportional to the molality* (m) *of the solution.*

$$\triangle T_f \propto m \qquad \text{or} \qquad \triangle T_f = k_f m \qquad \ldots \text{(XIV.15)}$$

where k_f, the proportionality constant, is called the *molal freezing point constant or the molal cryoscopic constant.*

Law II. *Equimolecular quantities of different solutes dissolved in the same quantity of a given solvent depress the freezing point to the same extent.*

Since the depression depends only on the molality *i.e.* the number of molecules of the solute and not on the nature of the solute, it is a colligative property.

But even if the concentration (m) be the same, the depression is different for different solvents. That is, the cryoscopic constant is different for different solvents.

These laws, commonly known as Raoult's laws for depression of the freezing point, are strictly valid for *dilute* solutions of non-volatile non-electrolytes.

For a solution of unit molality, $m = 1$, hence $k_f = \triangle T_f$. So, the molal depression constant, k_f, is the depression of the freezing point of a solution of unit molality. But one molal solution would be too concentrated to obey Raoult's Laws mentioned above. The value of k_f is mostly obtained from eqm. XIV.15, using a dilute solution of a known solute and measuring $\triangle T_f$. The values of the molal f. pt. depression constants of some solvents are given in the Table below.

TABLE: MOLAL DEPRESSION CONSTANTS

Solvent	*m.pt.* (°C)	k_f	*Solvent*	*m.pt.* (°C)	k_f
Water	0	1.86	Cyclohexane	6.5	20.2
Acetic acid	16.5	3.9	Naphthalene	80.2	7.0
Benzene	5.6	5.12	Camphor	—	40.0
Nitrobenzene	5.6	6.90	Pinene dibromide	—	81.0

14.9. Thermodynamic Derivation of the Laws of Freezing Point Depression

A quantitative relation between the concentration of the solution and the freezing point depression can be worked out thermodynamically using Raoult's law of lowering of vapour pressure. The solution being dilute is regarded as an ideal one.

The vapour-pressures at A and Q (Fig. XIV.10) are p_1^0 and p_s and both of them lie on the vap-pressure curve AC of the solid phase. Using Clausius-Clapeyron equation,

$$(a)\ \ln p_1^0 = -\frac{L_s}{R}\cdot\frac{1}{T_f} + Z; \quad \text{and} \quad (b)\ \ln p_s = -\frac{L_s}{R}\cdot\frac{1}{T_f'} + Z$$

where L_s = molar latent heat of sublimation and Z a constant.

$$\therefore \quad ln\frac{p_s}{p_1^0} = -\frac{L_s}{R}\left[\frac{1}{T_f'} - \frac{1}{T_f}\right] = -\frac{L_s}{R}\cdot\frac{\triangle T_f}{T_f^2} \qquad \ldots (A)$$

putting $T_f - T_f' = \triangle T_f$ and assuming $T_f.T_f' \approx T_f^2$.

Again, the vapour-pressures at Q and at R are p_s and p_1 and both of them lie on the vapour-pressure curve DE of the solution. From Clausius-Clapeyron equation,

$$(c)\ \ ln\, p_s = -\frac{L_v}{R}\cdot\frac{1}{T_f'} + Z_1 \qquad \text{and} \qquad (d)\ ln\, p_1 = -\frac{L_v}{R}\cdot\frac{1}{T_f} + Z_1$$

where Z_1 is a constant and L_v = molar latent heat of vaporisation.

$$\therefore \quad ln\frac{p_s}{p_1} = -\frac{L_v}{R}\left[\frac{1}{T_f'} - \frac{1}{T_f}\right] = -\frac{L_v}{R}\cdot\frac{\triangle T_f}{T_f^2} \qquad \ldots (B)$$

Subtracting (B) from (*A*),

$$ln\frac{p_1}{p_1^0} = -\frac{\triangle T}{RT_f^2}\left[L_s - L_v\right] = -\frac{L_f}{RT_f^2}\cdot\triangle T_f$$

since the molar latent heat of fusion of the solvent $L_f = L_s - L_v$.

Rewriting, $$ln\left(1 - \frac{p_1^0 - p_1}{p_1^0}\right) = -\frac{L_f}{RT_f^2}\triangle T_f$$

As $\frac{p_1^0 - p_1}{p_1^0}$ is quite small, expanding the logarithmic series,

$$\frac{p_1^0 - p_1}{p_1^0} = \frac{L_f}{RT_f^2}\triangle T_f$$

From Raoult's law of vap. pressure lowering, the mol-fraction of the solute,

$$x_2 = \frac{p_1^0 - p_1}{p_1^0},$$

$$\therefore \quad \frac{L_f}{RT_f^2}\triangle T_f = x_2 \quad \text{or} \quad \triangle T_f = \frac{RT_f^2}{L_f}x_2 \qquad \ldots (\text{XIV}.16)$$

That is, the depression in freezing point is proportional to the mol-fraction of the solute.

In dilute solutions, mol-fraction $x_2 \approx \frac{n_2}{n_1} = \frac{w_2/M_2}{w_1/M_1}$, when w_2 gm of solute are dissolved in w_1 gm of solvent. The mol-wts. of solute and solvent are M_2 and M_1.

Hence, $$\triangle T_f = \frac{RT_f^2.\, w_2M_1}{L_f\ \ w_1M_2} = \frac{RT_f^2}{l_f}\cdot\frac{w_2}{w_1M_2}\ ;\ (l_f = L_f/M_1)$$

$$\therefore \quad \triangle T_f = \frac{RT_f^2}{1000\times l_f}\left[\frac{w_2\times 1000}{w_1M_2}\right] \qquad \ldots (\text{XIV}.17)$$

That is, $$\triangle T_f = \frac{RT_f^2}{1000\times l_f}m, \qquad \ldots (\text{XIV}.18)$$

where the molality of the solution, $m = \frac{w_2 \times 1000}{w_1 \times M_2}$ (see eqn. XIV.8) and l_f is the latent heat of fusion per gm.

$$\therefore \qquad \triangle T_f = k_f . m \qquad \ldots \text{(XIV.19)}$$

where k_f is a constant for a given solvent equal to $\frac{RT_f^2}{1000 \times l_f}$. The constant k_f is the *molal depression constant or the molal cryoscopic constant.*

$$\text{Assuming } R \approx 2 \text{ cal}; \quad k_f = \frac{RT_f^2}{1000 l_f} = \frac{0.002 T_f^2}{l_f} \qquad \ldots \text{(XIV.20)}$$

Hence k_f can also be computed from the boiling point and latent heat of fusion of the solvent.

14.10. Measurement of Freezing Point Depression

(*i*) *Beckmann's Method.* A sketch of the apparatus used is given in Fig. XIV.11. A wide glass tube 'A' with a side arm B is taken with a known weight of the liquid solvent. The tube is fitted with a cork through which are introduced a Beckmann thermometer T and a stirrer S_1. The tube A is placed in a much wider tube C, which serves as an air-jacket. The entire thing is then kept immersed in a freezing mixture. There is also a stirrer S_2 to stir the freezing mixture.

The tube A is first directly put in freezing mixture to solidify the solvent. The tube is then slowly warmed in hand with continuous stirring till fully melted. It is then placed in the air jacket C and surrounded by freezing mixture. The solvent is stirred slowly; its temperature goes down steadily. The temperature actually goes somewhat below the freezing pt. due to unavoidable supercooling. But when the crystallisation just starts, the temperature jumps up and remains steady for a reasonable time. This steady temperature is recorded from the Backmann thermometer. A weighed pellet of solute is next added to the solvent through side arm B. The freezing point of the solution is again recorded as before. The difference of the two readings in the Beckmann thermometer gives the depression of the freezing point of the solution.

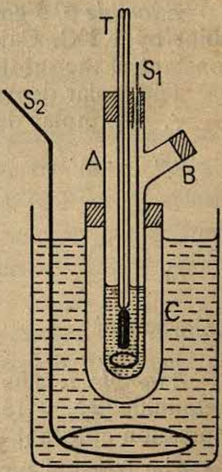


Fig. XIV.11
Beckmann's method for measuring f. pt. depression

(*ii*) *Rast's Method.* In this method camphor with its very high molal depression constant ($k_f = 40$) is used as solvent and as such the method is applicable to solutes like alkaloids which are soluble in molten camphor. Even for dilute solutions, the freezing point is considerably depressed and the lowering can be measured with ordinary thermometers. Usually the f-pt. of pure camphor is first determined and then a solute of known mol-wt. is added in known amounts to a definite wt. of camphor and melted. The mixture is cooled and powdered and subsequently melting point is determined. From this, the value of molal freezing point constant is obtained.

Once k_f is known for the camphor sample, it can be mixed with a definite weight of a solute of unknown mol-wt. and the freezing point determined by repeated melting and freezing. The mol-wt. of the solute can then be calculated from equation (XIV.17).

In this method other 'solvents' with high molal freezing constants are also used such as Borneol, hexachloro-ethane, tetrabromo-methane, camphor, quinone, etc. These solvents are solids at room temperature, the melting points of solvents or their solutions can be easily determined by the usual capillary method and very little quantity of substance is needed.

14.11. Determination of Mol wt. from freezing point depression.

The equation (XIV.19) is

$$\triangle T_f = k_f m$$

Substituting k_f from eqn. (XIV.20) and m from eqn. (XIV.8),

$$\triangle T_f = \frac{RT_f^2}{1000\, l_f} \cdot \frac{w_2 \times 1000}{w_1 \times M_2}$$

or the mol. wt. of the solute, $M_2 = k_f \dfrac{w_2 \times 1000}{\triangle T_f \times w_1}$ . . . (XIV.21)

Hence the mol. wt. M_2 can be obtained from a knowledge of k_f and a measurement of $\triangle T_f$.

Example 6. 5 gm of a substance dissolved in 50 gm water lowered the freezing point by 1.2°C. Calculate the mol. wt. of the substance. The molar depression constant of the substance is 18.5°C per 100 ml. of water. (Delhi Univ.)

The molar depression per 100 gm water is 18.5°C

∴ The molar depression per 1000 gm water is 1.85°C

i.e. $k_f = 1.85$

$$\triangle T_f = k_f \,.\, \frac{w_2 \times 1000}{w_1 \times M_2}$$

or $$1{\cdot}2 = 1{\cdot}85 \times \frac{5 \times 1000}{50 \times M_2}$$

whence $$M_2 = 154.2$$

Example 7. The m. pt. of phenol is 40°C. A solution containing 0.172 gm acetanilide ($M_2 = 135$) in 12.54 gm phenol freezes at 39.25°C. Calculate the molal depression constant and the latent heat of fusion of phenol.

The freezing point depression, $\triangle T_f = 40 - 39.25 = 0.75$; mol wt. $M_2 = 135$

Hence, $$K_f = \frac{\triangle T_f w_1 M_2}{w_2 \times 1000} = \frac{0.75 \times 12.54 \times 135}{0.172 \times 1000} = 7.38$$

Since $$K_f = \frac{RT_f^2}{l \times 1000} = \frac{2 \times (313)^2}{l \times 1000}$$

or, latent heat of fusion of phenol, $l = \dfrac{2 \times 313^2}{7.38 \times 1000} = 26.5$ calories per gm

Example 8. The freezing point of pure benzene = 5.44°C and that of a solution containing 2.092 gm of benzaldehyde in 100 gm of benzene is 4.44°C. Calculate the mol-weight of benzaldehyde, when K_f for benzene is 5.1.

$$\triangle T_f = \frac{w_2 \times 1000}{w_1 \times M_2} \,.\, K_f$$

or $$M_2 = \frac{w_2 \times 1000}{w_1 \times \triangle T_f} K_f = \frac{2.092 \times 1000}{100 \times (5.44 - 4.44)} \times 5.1 = 106.6$$

Example 9. A solution containing 2.423 gm of sulphur in 100 gm of naphthalene (m. pt. 80.1) gave a freezing point depression of 0.64°C. The latent heat of fusion of naphthalene is 35.7 calories per gm. What is the molecular formula of sulphur in the solution?

$$\triangle T_f = \frac{RT_f^2}{1000.l} \cdot \frac{w_2 \times 1000}{w_1 \times M_2}$$

or
$$0.64 = \frac{2 \times (353.1)^2}{1000 \times 35.7} \times \frac{2.423 \times 1000}{100 \times M_2}$$

whence,
$$M_2 = 264$$

But the atomic weight of sulphur is 32. So the mol-formula of sulphur is S_8.

D. OSMOTIC PRESSURE OF SOLUTIONS

14.12. Osmosis

In 1748, Abbe Nollet made the first striking observation that when a pig's bladder filled with alcohol and tied at the neck was kept immersed in water, it swelled enormously and ultimately burst. This is because the wall of the bladder is *semipermeable*, it allows water to get in but the alcohol cannot pass out.

In fact, there are membranes which are impervious to solute molecules but they allow solvent molecules to pass through them. These are called *semipermeable membranes*. Pig's bladder, intestinal walls of some animals, the inner walls of egg-shells, the potato-skin etc. are semipermeable membranes. Collodion, gelatine films, cellophane films etc. are also semipermeable. The best semipermeable membrane commonly used now is a layer of precipitated copper ferrocyanide deposited on a porous wall.

Now if a solution and pure solvent be kept separated by means of a semipermeable membrane, the solvent molecules only will pass through the membrane into the solution in order to dilute it. *This phenomenon of diffusion of a solvent through a semipermeable membrane from the solvent to a solution or from a dilute solution to a concentrated one is called osmosis*. Since the solute cannot diffuse through the membrane, nature tends to achieve equilibrium through osmosis. It is understood that the passage of solvent occurs in both directions, but the diffusion of the solvent from the solvent to the solution is much more rapid than that in the opposite direction.

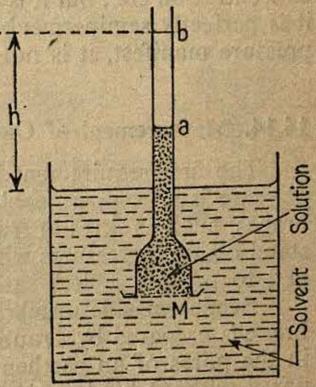


Fig. XIV.12

An easy demonstration can be made by tying a stretched piece of bladder or cellophane across the mouth of an inverted thistle funnel. It is filled with conc. sugar solution and kept partly immersed in water as in Fig. XIV.12. Slowly the liquid inside will rise and finally the level becomes stationary. This is because due to osmosis, the water from outside enters through the membrane, but when the hydrostatic pressure counterbalances the force which causes the water to diffuse from outside, the eqm. is attained and the level becomes stationary.

Other illustrations of osmosis may be cited. When a dry prune is placed in water, it swells as water enters through the semipermeable skin of the fruit. The hard outer shell of an egg may be removed by carefully dissolving it in dil. HCl. If the egg is then placed in water, it swells. On the other hand, if the egg is placed in very conc. solution of a salt, the egg shrinks. The thin membrane beneath the hard shell is semipermeable.

Red blood cells when placed in a conc. solution are found to shrivel when observed under microscope. But they swell and burst when kept in a very dilute solution, which is the cause for *haemolysis.*

14.13. Osmotic Pressure

Let us have a U-tube, as in Fig. XIV.13, provided with a semipermeable partition at the centre *X*. One arm of the tube is filled with a solution and the other with pure solvent. There are piston arrangements for applying pressures on the liquids. Normally solvent will pass through *X* into the solution *i.e.*, osmosis will occur. This diffusion of the solvent into the solution through the membrane can be counteracted by applying pressure π over the solution. The excess pressure π on the solution that would just prevent osmosis is called the osmotic pressure of the solution. The term is somewhat misleading, for a solution by itself cannot exert any pressure due to osmosis. *The osmotic pressure of a solution is the pressure required to prevent osmosis when the solution is separated from pure solvent by a semipermeable membrane.*

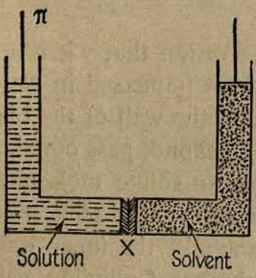


Fig. XIV. 13
Osmotic pressure

When eqm. is established between the two sides of the membrane the rates of diffusion of the solvent in the two opposite directions will be the same. The magnitude of the osmotic pressure depends on various factors such as temperature, concentration etc., but it is not dependent on the nature of the membrane provided it is perfectly semipermeable. Hence, although the membrane makes the osmotic pressure manifest, it is not the cause of the osmotic pressure.

14.14. Measurement of Osmotic Pressure

The first requirement in a study of osmosis or the measurement of osmotic pressure is a semipermeable membrane. Naturally occuring semipermeable membranes, such as skins of fruits, walls of animal organs, etc are two weak to withstand osmotic pressures which are often quite high. It was Traube who succeeded first to prepare a very satisfactory semipermeable membrane artificially.

Semipermeable membrane : One of the extensively used semipermeable membrane is prepared by Traube's method by depositing a ppt. of copper ferrocyanide in the pores of an earthenware pot. And earthenware porous pot, specially prepared without binders, is thoroughly cleaned, dried and finally soaked in water till the pores are filled with water. The pot is then placed in a 3% solution of $CuSO_4$ for a few hours. The interior of the pot is then washed and quickly dried. Next it is filled up with a 3% solution of potassium ferrocyanide and the pot is again placed in copper sulphate solution. The diffusion of the salts leads to a deposit of jelly-like precipitate of copper ferrocyanide in the pores of the walls of the pot.

In fact a membrane is formed inside the pores turning the pot into a cell of semipermeable walls. Sufficient time is allowed for any diffusion of salt to cease. The cell is then thoroughly washed free from all electrolytes and is ready for use. Nowa-days, copper ferrocyanide is electrolytically deposited by taking $CuSO_4$ solution inside the pot and $K_4Fe(CN)_6$ outside and passing a slow current, such that copper ions travel outwards and ferrocyanide ions inwards. These meet in the pores of the wall forming copper ferrocyamide deposit as before.

Pfeffer's Method: A semipermeable cell A, an earthenware porous pot with deposit of copper ferrocyanide, is cemented with a wide glass tube B. The tube B has a side-tube to which is attached a calibrated manometer (M) with N_2-gas enclosed above mercury. A diagrammatic sketch of the apparatus is given in Fig. XIV.14. The cell and the space up to mercury is filled up with the solution. The filling is made through a tube which is ultimately sealed off. The pot is placed in a bath of pure solvent at a constant temperature. As the solvent diffuses in, the pressure rises. When equilibrium is attained, the pressure is recorded from the manometer. The concentration of the solution may change to some extent due to entry of solvent but with a closed type manometer the dilution is indeed negligible. With such cells Pfeffer made extensive measurement of osmotic pressure of various solutions.

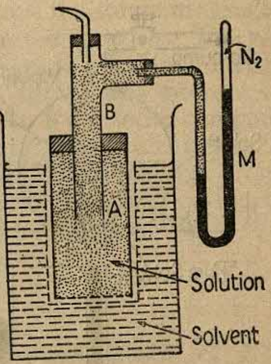


Fig. XIV. 14
Det. of osmotic pressure

Morse and Frazer's Method: Morse and Frazer improved Pfeffer's method though the principle was the same. They used a strong porous pot with electrically deposited copper ferrocyanide to serve as the semipermeable membrane. A sketch of their apparatus is given in Fig. XIV.15. The porous pot was sealed in an inverted position to an outer wider bronze cylinder. The porous pot was filled with water and the bronze cylinder with the solution. The outer cylinder was attached to a manometer from which the pressure could be measured, when the water level becomes steady.

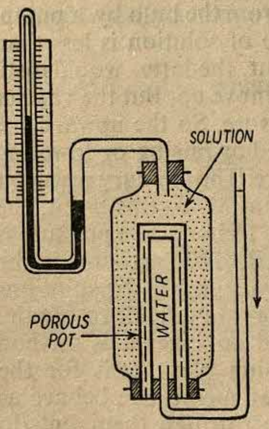


Fig. XIV. 15. Det. of osmotic pressure by Morse & Frazer method

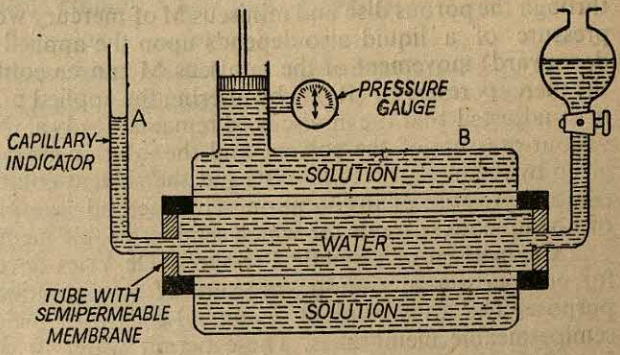


Fig. XIV.16 Det. of osmotic pressure (Berkeley and Hartley)

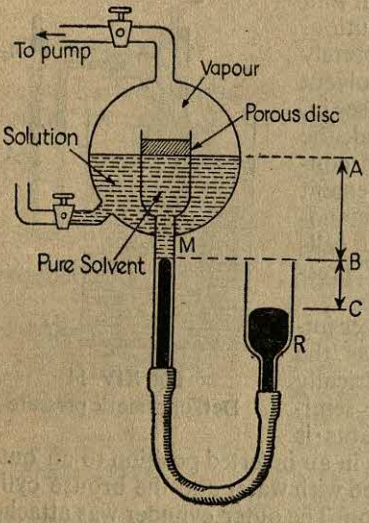
Berkeley and Hartley's Method: Berkeley and Hartley (1906) introduced a different technique in measuring osmotic pressure. In this method the solvent is not allowed to enter the solution but an external pressure is applied on the solution just enough to prevent inflow of solvent. This applied pressure is the osmotic pressure. An outline of the apparatus is shown diagrammatically in Fig. XIV.16.

The inner porcelain tube has electrically deposited copper ferrocyanide in the pores of its wall and serves as the semipermeable membrane. At one end of the tube is fitted a capillary tube A and at the other end there is a tube leading to a funnel through a stop cock. A much wider gum-metal tube B surrounds the inner tube and is tightly cemented to it. B is provided with a piston to which a pressure gauge is attached. The annular space between the two tubes is filled up with the solution, while inside the inner tube is introduced pure solvent up to a definite mark *A* in the capillary. A pressure is applied on the piston so that the solvent level in the capillary remains constant. This pressure recorded from the gauge is the osmotic pressure. The advantage of the method lies in its rapidity of determination and that the concentration of the solution remains unaltered.

Townsend's porous disc method: In this method, the usual semipermeable membrane is not used as such. The vapour of the solvent passing through the capillaries of a barrier serves the function of the semipermeable membrane. A sketch of the apparatus used is given in Fig. XIV. 17.

A porous disc is made from special clay and glass powder and it has very fine capillaries which allow only the vapour to pass. The disc is fitted to the mouth of a cylindrical funnel. The funnel itself is fused to a half-litre bulb containing the solution. Below the disc, there is pure solvent in the funnel, which extends to a column of mercury ending into a reservoir (R) of mercury.

Air is removed from the bulb by a pump. Since vapour pressure of solution is less than that of the pure solvent, the latter would distil through the porous disc and miniscus M of mercury would move up. But the vapour pressure of a liquid also depends upon the applied pressure. So the upward (or downward) movement of the miniscus M can be controlled by raising or lowering the mercury reservoir (R) *i.e.* by altering the applied pressure. The mercury reservoir is so adjusted that the miniscus M remains steady at the point M. At this point, the vapour pressure of the solvent and the solution are equal. The negative pressure is given by the mercury column BC and the solvent column AB. This pressure is the osmotic pressure of the solution. This method is especially suitable for solutions of nonaqueous solvents for which semipermeable membranes are diffcult to obtain.



(Fig. XIV.17. Townsend's porous disc method

Comparison of Osmotic Pressures. De Vries developed an ingeneous method for comparison of osmotic pressure of two solutions using plant cells for the purpose. The walls of plant or animal cells with their inner membrane behave as semipermeable membranes. These permit water to diffuse through them but do not allow the substances of the cell-sap such as sugar, salts etc. to come out. When such a cell is placed in a concentrated solution, the water of the cell passes outwards and the membrane of the cell wall shrinks; this is called **palsmolysis.** On the other hand, if the cell is placed in a dilute solution or in water, it swells. The shrinking or swelling can be clearly detected by observing them under the microscope, especially if the cells are stained.

The osmotic pressures of the two solutions were compared by finding out how much these had to be diluted to produced no effect—*i.e.*, no shrinking or swelling—on the cells. Such solutions which have no effect on the cell fluid are called **'isotonic'** solutions; these are in equilibrium with the cell-sap so far as their tensions are concerned. A 0.84 per cent NaCl solution is isotonic with the contents of our red blood cells and is usually called '*normal saline*'. Had the cell-membrane be perfectly semipermeable, isotonic solutions would also be isosmotic, that is, the two solutions would also have same osmotic pressure. The imperfect semipermeability of the cell-membranes means that isotonic solutions are not strictly isosmotic.

Mechanism of osmosis: Different explanations have been forwarded from time to time for the semipermeable nature of the membranes. The early idea that the pores of the membrane were not sufficiently big to permit the solute molecules to pass was discarded for the simple fact that the membranes were also impervious to solute molecules which were definitely known to be smaller in dimensions compared to the solvent molecules. In other theories, the solvent molecules are supposed to be soluble in the membrane material, or to form loose compounds with the membrane molecule or adsorbed in the capillaries of the membrane. It is yet difficult to say very definitely anything regarding the mechanism of semipermeability. The solution has a lower vapour pressure than that of the pure solvent and the process of the solvent passing into the solution involves probably the distillation through the capillaries of the membrane.

14.15. Laws of Osmotic Pressure

The wealth of data which accummulated from the experiments of Pfeffer, of Morse and Frazer, of Berkeley and Hartley and their co-workers led to certain very interesting conclusions. It was realised quite early that the osmotic pressure of solutions depends upon both the temperature and the concentration of the solutions. Quantitatively these were formulated into the following laws:

Law I. *Temperature remaining constant, the osmotic pressure* (π) *of a solution is directly proportional to its concentration* (C).

$$\pi = k_1C, \qquad (k_1 \text{ is a constant})$$

Since $C = 1/v$, where v litres contain 1 gm-mole of solute,

$$\pi = k_1/v \quad \text{or} \quad \pi v = k_1$$

Law II. *Concentration remaining constant, the osmotic pressure* (π) *of a solution is directly proportional to absolute temperature* (T)

$$\pi = k_2T, \qquad (k_2 \text{ is a constant})$$

It is evident that these two laws are analogous to the Boyle's and Charle's laws for gas-pressures. Below are appended some experimental data which establish the validity of these laws.

TABLE: OSMOTIC PRESSURE AND CONCENTRATION OF SUCROSE SOLUTIONS (0°C)

(Berkely and Hartley)

molar Conc. C	Osmotic pressure π (atm)	Ratio π/C
0.0292	0.655	22.145
0.0584	1.310	22.420
0.0970	2.180	22.474
0.132	2.952	22.430

TABLE: OSMOTIC PRESSURE OF SUCROSE SOLUTIONS (0.1 molal)

Temp. (T°K)	π (*osmotic pressure*)	$\pi/T(\times 10^3)$
273	7.085	2.594
283	7.334	2.591
293	7.605	2.595
298	7.729	2.594

The two laws enunciated above may be combined, so as to give the relation

$$\pi = CKT$$

when both temperature and concentration would vary. K is a constant. If the solution contains n gm-moles of solute in V litres of solution, we have

$$\pi = \frac{n}{V}KT \quad \text{or} \quad \pi V = nKT \qquad \text{. . . (XIV.22)}$$

It may then be stated: *Equimolecular quantities of different solutes dissolved in the same volume of a solvent exert equal osmotic pressure at the same temperature.* It is presumed that the solutes are supposed not to suffer dissociation or association in the solution. This is sometimes mentioned as the third law for osmotic pressures.

As equimolecular quantities contain the same number of molecules, the above statement may be expressed alternatively: *Equal volumes of different solutions which are at the same temperature and exert same osmotic pressure contain an equal number of solute molecules.* This is indeed Avogadro's law applied to solutions. The osmotic pressure is thus dependent on the number of molecules and independent of their nature. So it is a colligative property.

The remarkable identity of equation XIV.22 with the ideal gas equation was pointed out by van't Hoff.

Ideal gas equation: $PV = nRT$
Osmotic pressure equation: $\pi V = nKT$

When the experimental values of π were substituted in equation XIV.22 the numerical value of K was found to be 0.082 litre-atmosphere/degree, the same as that of R of the gas equation. Equation XIV.23 for solutions now becomes, (C is the molar concentration of the solute in the solution),

or

$$\left.\begin{aligned}\pi V &= nRT\\ \pi &= CRT\end{aligned}\right\} \qquad \text{. . . (XIV.23)}$$

Van't Hoff therefore rightly stated: *The osmotic pressure of a substance in solution is the same as it would exert if it existed as a gas in the same volume as that occupied by the solution at the same temperature.* The solution is dilute and the volume occupied by the solute in solution is negligible compared to the volume of the solution.

This is generally called *van't Hoff's law of osmotic pressure*, which is really a combination of the separate laws stated earlier.

14.16. Thermodynamic Derivation of the Laws of Osmotic Pressure

Suppose a large reservoir of pure solvent having vapour pressure p_1^0 is placed by the side of another reservoir containing a solution having vapour pressure p_1. It is known $p_1^0 > p_1$; both resorvoirs are at the same temperature, T.

Let a small amount $\triangle x$ moles of pure solvent be vaporised reversibly at constant temperature T by keeping the pressure infinitesimally smaller than p_1^0. Since the process is carried out isothermally reversibly at constant pressure, the free energy change,

$$\triangle G_1 = vdp - SdT = 0$$

Next, the $\triangle x$ moles of solvent vapour is placed in a cylinder with a piston and expanded isothermally and reversibly until the pressure falls to p_1. The free energy change,

$$\triangle G_2 = \triangle x\, RT\, ln\, p_1/p_1^0$$

Finally, the vapour ($\triangle x$ moles at pressure p_1) is condensed reversibly and isothermally to the reservoir containing the solution. For this isothermal isobaric reversible condensation,

$$\triangle G_3 = vdp - SdT = 0$$

Hence, the net free energy change for the isothermal dilution of the solution by $\triangle x$ moles of solvent is

$$\triangle G = \triangle x RT\, ln\, p_1/p_1^0 \qquad \ldots \text{(XIV.24)}$$

Due to the very large volume of the reservoir, ($\triangle x$ is too small) the change in concentration of the solution is negligible.

Such dilution of the solution can be effected in other ways and the free energy change would be the same provided the processes be always reversible.

Suppose the solution reservoir be kept separated from the pure solvent by a semipermiable membrane along one wall. Let the pressure on the solution be P and that on the pure solvent be P', so that diffusion of solvent through the membrane is just prevented. That is, the osmotic pressure, of the solution.

$$\pi = P - P'$$

By keeping the pressure over the solution infinitesimally smaller than P, allow $\triangle x$ moles of solvent to diffuse into the solution through the membrane reversibly and isothermally. If $\bar{V}_1$ be the molar volume of the solvent, then the volume entering the solution is $\triangle x\bar{V}_1$.

The free energy for this process of dilution is

$$\triangle G = \int_P^{P'} \triangle x\bar{V}_1 dP = \triangle x\bar{V}_1(P' - P) = -\triangle x\pi\bar{V}_1 \qquad \ldots \text{(XIV.25)}$$

assuming $\bar{V}_1$ to remain constant.

Both the equations (XIV.24) and (XIV.25) represent the free energy change for the same reversible dilution of the solution by $\triangle x$ moles of solvent, then

$$-\triangle x\pi\bar{V}_1 = \triangle xRT\, ln\, p_1/p_1^0 = -\triangle xRT\, ln\, \frac{p_1^0}{p_1}$$

or $$\pi\bar{V}_1 = RT\, ln\, p_1^0/p_1 \qquad \ldots \text{(XIV.26)}$$

This is the thermodynamic *relation between osmotic pressure and vapour pressure.* It can be rewritten as

$$\pi\bar{V}_1 = -RT\, ln\, p_1/p_1^0 = -RT\, ln\, [1-(p_1^0-p_1)/p_1^0]$$

or $$\pi\bar{V}_1 = RT\frac{p_1^0-p_1}{p_1^0}, \qquad \text{since } (p_1^0-p_1)/p_1^0 \text{ is quite small.} \qquad \ldots \text{(XIV.27)}$$

or $$\frac{p_1^0-p_1}{p_1^0} = \frac{\pi\bar{V}_1}{RT} = \frac{\pi M_1}{\rho RT} \qquad \ldots \text{(XIV.28)}$$

where M_1 and ρ are the mol. wt. and density of the solvent. This correlates osmotic pressure with relative lowering of vapour pressure.

Since from Raoult's Law, $\frac{p_1^0-p_1}{p_1^0} = x_2$ (mol-fraction of solute) equation (XIV.27) gives

$$\pi\bar{V}_1 = RTx_2 = \frac{n_2}{n_1+n_2}RT \approx \frac{n_2}{n_1}RT \text{ (for dilute solutions)}$$

or $\pi = \frac{n_2}{n_1\bar{V}_1}RT = \frac{n_2}{v}RT$, ($v$ = volume of n_1 moles of solvent containing n_2 moles solute)

or $\pi = CRT$, where molar conc. $C = n_2/v$

This is the same van't Hoff's relation for osmotic pressure mentioned earlier.

14.17. Molecular weight from osmotic pressures

The equation for osmotic pressure (XIV.23) $\pi = CRT$ may be written as

$\pi = \frac{w_2}{M_2v}RT$ where w_2 gm solute (mol. wt. M_2) is dissolved in v litres.

or $$M_2 = \frac{w_2}{\pi v}RT \qquad \ldots \text{(XIV.29)}$$

Thus from a knowledge of the osmotic pressure of a given solution, the mol. wt. of the solute can be found out.

Example 10. What is the osmotic pressure of a 5% aqueous cane sugar solution at 15°C? (Punjab Univ.)

$$M_2 = 342, \quad v = 0.1 \text{ litre}, \quad w_2 = 5, \quad T = 288°K$$

$$\therefore \quad \pi = \frac{w_2}{M_2v}RT = \frac{5}{342\times 0.1}\times 0.0821\times 288$$

$$= 3.45 \text{ atm.}$$

Example 11. Estimate the concentration of a sugar solution which has an osmotic pressure of 2.51 atm at 24°C?

$$\pi = 2.51 \text{ atm.} \quad T = 297°\text{K}$$

$$\therefore \quad C = \frac{\pi}{RT} = \frac{2.51}{0.082\times 297} = 0.1029 \text{ moles/litre.}$$

Example 12. Calculate the mol. wt. of urea. 0.184 gm urea when dissolved in 100 c.c., the solution has an osmotic pressure of 56 cm (*Hg*) at 30°C.

$$\pi = 56/76 \text{ atm}, \quad T = 303°\text{K}, \quad v = 0.1 \text{ litre}, \quad w_2 = 0.184 \text{ gm}.$$

$$M_2 = \frac{w_2 RT}{\pi v} = \frac{0.184\times 0.082\times 303}{(56/76)\times 0.1} = 62.1$$

Example 13. A solution containing 10.2 gm of a substance per litre is found to be isotonic with a 2% solution of glucose ($M = 180$). Calculate the mol. wt. of the substance. Both are at the same temperature.

Let π be the common osmotic pressure and let M' be the molecular weight of the substance. The temperature is T°K.

Then (*i*) for glucose: $\pi = \frac{w_2}{M_2 v} RT = \frac{2}{180\times 0.1} \times RT$

(*ii*) for the substance: $\pi = \frac{w'}{M'\times v'} \times RT = \frac{10.2}{M'\times 1} RT$

$$\therefore \quad \frac{10.2}{M'} = \frac{2}{180\times 0.1} \quad \text{or} \quad M' = \frac{10.2\times 18}{2}$$

whence $M' = 9.18$

14.18. Inter-relations between different colligative properties

(*a*) The relation between osmotic pressure and vapour-pressure lowering has already been deduced in equation (XIV.28),

$$\frac{\triangle p}{p_1^0} = \frac{\pi M_1}{\rho RT} \quad \text{. . . (XIV.28)}$$

(*b*) The elevation of b. pt. ($\triangle T_b$) (is given by equation (XIV.9),

$$\triangle T_b = k_b \frac{w_2\times 1000}{M_2\times w_1} = k_b \frac{n_2\times 1000}{n_1\times M_1}; \quad (\because w_1 = n_1 M_1)$$

or

$$\triangle T_b = k_b \frac{1000}{M_1} x_2 \quad \text{. . . (XIV.30)}$$

Since $x_2 = \triangle p/p_1^0$, hence $\triangle T_b = k_b \frac{1000}{M_1} \frac{\triangle p}{p_1^0}$ . . . (XIV.31)

This is the relation between b.pt. elevation and vapour pressure lowering.

(*c*) Since $x_2 = \triangle p/p_1^0 = \frac{\pi M_1}{\rho RT}$,

$$\therefore \quad \triangle T_b = k_b \frac{1000}{M_1} \cdot \frac{\pi M_1}{\rho RT} = \frac{k_b \times 1000}{\rho RT} \pi , \qquad \ldots (XIV.32)$$

a relation between osmotic pressure and b. pt. elevation.

Similarly for f. pt. depression,

$$\triangle T_f = k_f \frac{1000}{M_1} \frac{\triangle p}{p_1{}^0} \qquad \ldots (XIV.33)$$

and

$$\triangle T_f = \frac{k_f \times 1000}{\rho RT} \pi \qquad \ldots (XIV.34)$$

Example 14. The vapour pressure of a 1 molar sucrose solution in water is 31.207 mm at 30°C, when pure water has the vapour pressure of 31.824 mm. The density of pure water is 0.9956 gm/c.c. Calculate its osmotic pressure.

From equation (XIV.26),

$$\pi = \frac{RT}{\bar{V}_1} ln \frac{p_1{}^0}{p_1} = \frac{0.0821 \times 2.303 \times 303}{0.018} \log \frac{31.824}{31.207}$$

$$\text{(since } \bar{V}_1 = \frac{M}{\rho} = \frac{18.00}{0.9956} = 18.01 \text{ c.c.} = 0.018 \text{ lit/mole.)}$$

whence $\pi = 26.9$ atm.

Example 15. At 100°C the vapour pressure of a solution of 6.5 gm of a solute in 100 gm water is 732 mm. What is the boiling pt. of the solution? ($K_b = 0.52$). Assume the laws of dilute solution.

At 100°C, for pure water $P_0 = 760$ mm

$$\triangle P = P_0 - P = 760 - 732 = 28 \text{ mm}$$

Hence

$$\frac{n_2}{n_1} = \frac{\triangle P}{P_0} = \frac{28}{760}$$

Now

$$\triangle T_b = K_b \frac{\omega_2 \times 1000}{\omega_1 \times M_2} = k_b \frac{n_2 . 1000}{n_1 M_1}, \text{ (Since } n_2 = \frac{\omega_2}{M_2}; w_1 = n_1 M_1)$$

$$= 0.52 \times \frac{28}{760} \times \frac{1000}{18} = 1.064°$$

∴ The boiling-pt. of the solution, $T_b = 101.064$°C

Example 16. Calculate the freezing point of a solution of cane sugar which has an osmotic pressure of 5 atmospheres at 50°C.

From equation (XIV.34),

$$\pi = \frac{\rho RT . \triangle T_f}{1000 \times K_f} = \frac{1 \times 82 \times 323 \times \triangle T_f}{1000 \times 1.86}$$

or

$$\triangle T_f = \frac{5 \times 1.86}{0.082 \times 323} = 0.352, \text{ (using } R \text{ in c.c. atm, as } \rho \text{ is gm/c.c.)}$$

The freezing pt. of the solution is −0.352°C.

14.19. Abnormal Behaviour of Solutions

The experimental results for the colligative properties of solutions often vary from the values calculated from the relations mentioned above. This is due to two reasons.

I. Non-ideality of Solutions: The laws for dilute solutions are basically derived from the Raoult's Law, $p_i = x_i p_i^0$. Raoult's law is valid for ideal solutions only. But real solutions obey Raoult's law only at high dilutions. At high concentrations, the solutions exhibit considerable departure from the Raoult's law. The laws for elevation of b. pt., f. pt.-depression and osmotic pressure would hence be applicable in the dilute range where Raoult's law is obeyed. For example, the molecular weight of nitrobenzene is derived from depression of freezing pt. of benzene. The value experimentally obtained is 124.5 when 0.10 molar solution is taken and the value is above 150 when 1 molar solution is taken. The true mol. wt. is 123.

The element of non-ideality also enters into the picture when solvent and solute molecules affect each others' intermolecular forces, or, if there be association or complex-formation between them. These become quite conspicuous at higher concentrations.

II. The association or dissociation of solute molecuels also leads to departure from the theoretical expectations.

Association in Solution. Some solutes when dissolved in non-hydroxylic solvents like benzene, cyclohexane, carbon-tetrachloride, nitrobenzene etc. remain associated. Thus, carboxylic acids like acetic acid, benzoic acid etc. remain mostly as dimers in benzene solution. The association would render the number of solute particles less than what it would have been if the solute were present as single molecules. The properties of dilute solutions, being colligative in nature, depend on the number of solute particles and not one their chemical composition. In consequence, the values of osmotic pressure, freezing point depression, etc. would be less than those theoretically anticipated from the relations derived for them. The molecular weight calculated from the observed freezing point lowering or boiling point elevation etc. in such cases would obviously be higher. The observed values for the mol. wt. of acetic acid obtained from freezing point depression are given in the table here, which show that except in very dilute solutions, the molecular weight is nearly double that of its chemical formula (mol. wt. 60).

TABLE: OBSERVED MOL. WT. OF ACETIC ACID IN BENZENE SOLUTION

Molality	$\triangle T_f$(°C)	*Obs. mol. wt.*	M_{obs}/M_{theo}
0.003	0.016	65.8	1.09
0.015	0.054	84.5	1.41
0.097	0.254	117.0	1.95
0.510	1.252	114.5	2.07
1.025	2.410	130.2	2.17

It is clear that at very high dilutions only acetic acid remains as single molecules in benzene solutions; at low dilutions most of the acid remain as dimers. At fairly high concentration, the degree of association even exceeds 2. This is due to the fact that apart from association, the solution also shows positive deviation from Raoult's law to some extent.

The degree of association can also be evaluated. Suppose α is the degree of association *i.e.*, the fraction of total solute present as dimers of mol. wt. $2M_0$. Then $(1-\alpha)$ fraction would remain as single molecules of mol. wt. M_0. If M is the mean (observed) mol. wt., then

$$M\left(1-\alpha+\frac{\alpha}{2}\right) = 2M_0\left(\frac{\alpha}{2}\right) + M_0(1-\alpha)$$

or

$$\alpha = \frac{2(M-M_0)}{M} \qquad \ldots \text{(XIV.20)}$$

If n molecules are associated, instead of 2, the degree of association would similarly be given by,

$$\alpha = \frac{n(M-M_0)}{M(n-1)} \qquad \ldots \text{(XIV.21)}$$

The finding of a higher value for mol. wt. from a colligative property does not necessarily mean association of the solute molecules in solution. This may be illustrated in the case of nitrobenzene.

Dissociation in Solution. In 1885, Van't Hoff found that dilute aqueous solutions of electrolytes such as NaCl, $MgSO_4$ etc. show a considerable departure from the ideal. The observed osmotic pressure of solutions of salts of known concentration (C) was found to be much higher than that predicted from the relation, $\pi = CRT$. In consequence, the mol. wt. calculated from the observed osmotic pressure was much less than the true value. Van't Hoff did not offer any explanation of the abnormal results. He introduced a factor 'i' to contain the deviations from ideal equation for solutions of electrolytes, expressing

$$\pi_{\text{ideal}} = CRT \qquad \text{and} \qquad \pi_{\text{observed}} = i.\ CRT$$

so that

$$i = \frac{\pi_{\text{obs}}}{\pi_{\text{ideal}}} \qquad \ldots \text{(XIV.35)}$$

The *Vant Hoff factor* 'i' is the ratio of observed osmotic pressure and the theoretically calculated or ideal osmotic pressure.

Further, for a given solution, the deviation in any colligative property was found to be the same, *i.e.*,

$$i = \frac{\pi_{\text{obs}}}{\pi_{\text{theo}}} = \frac{\triangle T_{f(\text{obs})}}{\triangle T_{f(\text{theo})}} = \frac{\triangle T_{b(\text{obs})}}{\triangle T_{b(\text{theo})}} = \frac{\triangle p_{(\text{obs})}}{\triangle p_{(\text{theo})}} \qquad \ldots \text{(XIV.36)}$$

Hence,

$$\pi\,(\text{obs}) = i\,\pi\,(\text{theo}) = i.\ CRT \qquad \ldots \text{(XIV.37)}$$

or

$$\triangle T_f\,(\text{obs}) = i\,\triangle T_f\,(\text{theo}) = i.\ k_b\,\frac{w_2 \times 1000}{w_1 \times M_2}\ \text{etc.}$$

In high dilutions, 'i' tends to the numerical value *two* for electrolytes like, NaCl, HNO_3, $MgSO_4$, etc. For electrolytes like H_2SO_4, $CoCl_2$, etc., the value approximates *three* and so on, as shown in table next page.

TABLE: van't Hoff factor '*i*' from obs. ΔT_f for different electrolytes

Electrolyte	*molality*			
	1.00	0.10	0.01	0.001
NaCl	1.81	1.86	1.94	1.97
HCl	2.12	1.89	1.94	1.98
HNO_3	1.92	1.89	1.96	1.97
H_2SO_4	2.17	2.12	2.46	2.82
$CoCl_2$	—	2.62	2.75	2.90
$Pb(NO_3)_2$	1.31	2.13	2.63	2.89
$K_3Fe(CN)_6$	—	2.85	3.36	3.82

The explanation of the abnormal colligative properties of solutions of electrolytes comes readily from the Arrhenius dissociation theory. According to the dissociation theory, the electrolyte molecules in solution break up into positive and negative ions. In very high dilutions, the dissociation is complete. Thus in dilute solutions, p molecules of NaCl will give rise to $2p$ ions; p molecules of H_2SO_4 will give $3p$ ions and so on. Since the colligative properties depend on the units of solute present in solution irrespective of their chemical nature and because, due to ionisation the number increases, the values of the colligative properties observed are much higher. In fact, these results from the dilute solutions gave the strongest and most dramatic support to the Arrhenius theory of dissociation.

Generally speaking, suppose a molecule breaks up into n ions in a given solution of concentration c. If α is the degree of dissociation, then

conc. of undissociated molecules $= (1-\alpha)c$

and conc. of (dissociated) ions $= n.\alpha.c$

Hence total conc. of solute particles $= c\,[1 + \overline{n-1}\,\alpha]$

The osmotic pressure of such a solution, $\pi_{obs} = c[1 + (n-1)\alpha]RT$. But from eqn. (XIV.37) van't Hoff's corrected equation is, $\pi_{obs} = i.cRT$

Hence
$$i = 1 + (n-1)\alpha$$

or
$$\alpha = \frac{i-1}{n-1} \qquad \text{...(XIV.38)}$$

As '*i*' is experimentally determined from freezing pt. measurement or measurement of other colligative properties, α is known. The degree of dissociation determined in this way is found to be practically the same as obtained from conductance measurements. Such identity confirms the explanation given above.

So, also,

$$\Delta T_f = k_f \frac{w_2 \times 1000}{w_1 \times M_2}[1+(n-1)\alpha]. \text{ etc.}$$

Example 17. A solution containing 4.13 gm LiCl per litre freezes at −0.343°C. Calculate van't Hoff factor and the degree of dissociation.

$$M_{LiCl} = 42.5, \quad \triangle T_f = 0.343°, \; n = 2$$

Calculated $$\triangle T_f = k_f.m = 1.86 \times \frac{4.13}{42.5}$$

$$\therefore \quad i = \frac{\triangle T_{f\ obs}}{\triangle T_{f\ theo}} = \frac{0.343 \times 42.5}{1.86 \times 4.13} = 1.898$$

The degree of dissociation, $\alpha = (i-1)/(n-1) = i-1 = 0.898 = 89.8\%$

Example 18. A 0.2 molal aqueous solution freezes at −0.68°C. Calculate *i* and the osmotic pressure at 0°C. ($k_f = 1.86$).

$\triangle T_f = i.k_f.m$; or $0.68 = i \times 1.86 \times 0.2$

whence $i = 1.83$

Osmotic pressure $\pi = icRT$

$= 1.83 \times 0.2 \times 0.082 \times 273$

$= 8.2$ atm

EXERCISES

I

1. Calculate the vapour pressure at 100°C of a solution containing 15.6 gm water and 1.68 gm of sucrose, $C_{12}H_{22}O_{11}$. (Osmania Univ.) [Ans. 717 mm]

2. At 28°C, the vapour pressure of a solution containing 13 gm solute in 100 gm water was 27.371 mm, when pure water had a vapour pressure of 28.065 mm. Calculate the mol. wt. of the solute. [Ans. 92.3]

3. In 90 gm of water were dissolved 1.2 gm urea and 1.71 gm sucrose. What will be the vapour pressure of this solution, that of pure water at the same temperature being 23.760 mm? [Ans. 23.614 mm]

4. A solution containing 25.00 gm of a sugar per 100 c.c. of water has a vapour pressure of 18.06 mm at *t*°C when pure water has a vapour pressure of 18.15 mm. Calculate the mol. wt. of the sugar. (Cal. Univ.) [Ans. 180.6]

5. Pure and dry N_2-gas was bubbled through a solution of 2.25 gm of a non-volatile solute (*A*) in 150 gm benzene and then through pure benzene. The loss in weight of the solution was 2.1540 gm and that of benzene 0·0160 gm. Calculate mol. wt. of A.

6. A solution was prepared by dissolving 10 gm of a non-volatile substance in 200 gm benzene. When a stream of air is passed through the solution, the solution lost 2.66 gm in weight. When the same volume of air was passed through pure benzene, the loss in weight was 2.80 gm. What is the mol. wt. of the solute? (Calicut Univ.) [Ans. 78]

II

7. The boiling point is raised by 0.472°C when 2.78 gm benzophenon is dissolved in 55.6 gm acetone ($k_b = 1.72°$). Calculate the mol. wt. of benzophenon. (Delhi Univ.) [Ans. 182.2.]

8. 0.7269 gm camphor ($M = 152$) was dissolved in 32.08 gm acetone. The solution boils at 56.55°C, when pure acetone boils at 56.30°C. Find out the k_b-value for acetone and also its latent heat of vaporisation. [Ans. $k_b = 1.677$, $l = 129.3$ cal/gm]

9. What will be the b.pt. of a solution containing 30 gm diphenyl ($M = 154$) in 250 gm benzene? (Given $k_b = 2.6$, b.pt. of benzene $= 80.1$°C) [Ans. 82°C]

10. A solution of 2.4 gm of a substance in 25.0 gm of water boils at 100.832°C at 1 atm. Calculate the mol. wt. of the substance. (Given k_b for water 5.2°C per 100 gm). (Kerala Univ.) [Ans. 60]

11. The boiling point of ether is 36°C. A solution of 1.6 gm naphthalene ($C_{10}H_8$) in 20 gm ether boils at 36.31°C. Calculate k_b and the lalent heat of vaporisation of ether per gm. [Ans. $k_b = 2.1$, $l = 90.4$ cal]

12. 3 gm of A dissolved in 500 gm of benzene raises the boiling point by 0.0912°C. Calculate the mol. wt. of A if l_v of benzene $= 94.4$ cal/gm and its boiling point be 80.2°C [Ans. 174]

III

13. 0.142 gm naphthalene ($C_{10}H_8$) in 20.25 gm benzene lowered the freezing point by 0.284°C. Find out the mol. wt. of naphthalene. ($k_f = 5.0$ for benzene). [Ans. 126.2]

14. 5 gm of a substance dissolved in 50 gm water lowered the freezing point by 1.2°C. Calculate the mol. wt. of the substance. The molal depression constant is 18.5°C for 100 c.c. water. (Delhi Univ.) [Ans. 154.2]

15. Equal volumes of two aqueous solutions, one containing 36 gm glucose ($C_6H_{12}O_6$) in 1000 gm water and the other 36 gm urea in 1000 gm water are mixed. What will be the f.pt of the resulting solution? The heat of fusion of ice is 80 cal/gm at 0°C. (Cal. Univ.) [Ans. −0.74°C]

16. A solution of 6 gm benzoic acid in 80 gm benzene shows a f.p. depression of 1.512°C. If cryoscopic constant of benzene be 4.9°, comment on the nature of existence of the acid in benzene solution. [Ans. $M_{calc} = 243$. But the true value is 122. Hence the acid is present as dimers in solution.]

17. A sample of camphor ($k_f = 40$) melts a 176°C. A solution of 0.0205 gm of a hydrocarbon in 0.261 gm camphor melts at 156°C. The hydrocarbon contains 92.3% carbon. Determine the mol. formula of the hydrocarbon. [Ans. $C_{12}H_{12}$]

18. A mixture of 1 gm naphthalene ($M = 128$) and 10 gm camphor freezes at 147°C where as pure camphor freezes at 177.5°C. What is the cryoscopic constant of camphor?

The m. pt. of a mixture of 1 gm acetanilide and 10 gm camphor ($M = 152$) is 148.5°C. What is the mol. wt. of acetanilide? [Ans. 39.04°C; 134.6]

IV

19. Calculate the mol. wt. of a substance 10 gm of which in 1000 c.c. solution exerts an osmotic pressure of 3 mm of Hg at 25°C. [Ans. 61990]

20. A solution of 1.73 gm A in 100 c.c. water is found to be isotonic with 3.42% solution of sucrose. Calculate mol. wt. of A. (Cal. Univ.) [Ans. $M = 173$]

21. At 17°C, estimate the osmotic pressure of a solution 150 c.c. of which contains 1.75 gm sucrose ($C_{12}H_{22}O_{11}$). [Ans. 0.81 atm]

22. At 20°C, the osmotic pressure of a solution containing 34.2 gm sucrose per litre is 2.522 atm. Compute the value of R. (Cal. Univ.) [Ans. 0.086 litre-atm]

23. At what temperature will a 5% solution of glucose ($M = 180$) develop an osmotic pressure of 7 atm? [Ans. 33.3°C]

24. In what volume of water should 20 gm of urea ($M = 60$) be dissolved to give an osmotic pressure of 1.2 atm at 35°C? [Ans. 7.02 litre]

V

25. The osmotic pressure of a 3% aqueous solution of A at 25°C is 3.632 atm. What is the vapour pressure of this solution? The vapour pressure of pure water at 25°C is 23.7 mm. [Ans 23.64 mm]

26. An aqueous solution has an osmotic pressure 2.51 atm at 25°C. What will be the f. pt. of the solution (k_f = 1.86 for water)? [Ans $T_f = -0.191°C$]

27. A solution of '*A*' in water has a freezing point of −0.45°C. Find out the boiling point of this solution. (For water $K_f = 1.86$, $k_b = 0.51$). [Ans. $T_b = 100.124°C$]

28. Calculate the freezing point of a solution of 1.1 gm acetic acid in 20 gm benzene. 95% acetic acid remains as dimers in this solution; f. pt. of benzene is 5.53 and k_f=5.0°C. [Ans. 3.084°C]

29. A solution of 3.6 gm A in 150 c.c. water has an osmotic pressure of 4.48 atm at 17°C. What is the boiling pt. of the solution (k_b = 0.52°C)? [Ans. 100.098°C]

30. Calculate the freezing point of 1.11 gm/litre aqueous solution of $CaCl_2$ (k_f = 1.86°C) [Ans. −0.0186°C]

31. Calculate the degree of dissociation in the following aqueous solutions:

(*a*) A 0.01 molal solution of $K_3Fe(CN)_6$ freezing at −0.06°C

(*b*) A 0.1 molal solution of a salt AB freezing at −0.204°C (k_f = 1.86°C) [Ans. 74.2%;9.7%]

32. The f. pt. of a 0.01 molal solution of $BaCl_2$ in water is −0.05°C. Estimate the vapour pressure of this solution at 25°C, if that of pure water is 23.756 mm. [Ans. −23.744 mm]

VI

33. "The behaviour of dilute solutions is similar to that of perfect gases."—Discuss.

34. Write brief notes on: (*a*) plasmolysis (*b*) isotonic solutions (*c*) cryoscopic constant (*d*) van't Hoff factor (*e*) semipermeable membrane.

35. Critically examine the following statements:

(*i*) Relative lowering of the vapour pressure of a dilute solution is proportional to the temperature of the system.

(*ii*) Two solutions of common salt and cane sugar at the same temperature had the same osmotic pressure, hence their concentrations shall also be the same.

(*iii*) In determining mol. wt. by freezing point method, camphor is preferred as a solvent because it does not chemically react with solutes.

(*iv*) In the experiments of f. pt. lowering, the solvent and the solute solidify together at the freezing pt. of solution.

CHAPTER 15

THE DISTRIBUTION LAW

15.1. The Distribution Law

Consider a system of two immiscible liquids in contact, say water and chloroform, to which a little quantity of iodine is added. Iodine will dissolve partly in water and partly in chloroform. The two solutions will separate into two layers. At eqm. the concentrations of iodine in the two layers would be different but their ratio is fixed independent of the quantity of iodine added or the volumes of the two liquids present.

Such a constancy of the ratio of concentrations is also observed with other solutes dissolving in different pairs of immiscible liquids, e.g., succinic acid between water and ether, $HgBr_2$ between water and benzene etc. From an extensive study of such systems, Nernst established a general principle, stated as:

At a constant temperature, the concentrations of a solute distributed between two liquids at eqm. bear a fixed ratio. This is known as the **Nernst Distribution Law.**

If C_1 and C_2 be the concentrations of the solute in the two immiscible liquids, then

$$\frac{C_1}{C_2} = K \qquad \ldots \text{(XV.1)}$$

The constant K is called the **Distribution coefficient** or **Partition Coefficient** of the solute between the two solvents at the given temperature. The value of K changes to some extent with change in temperature.

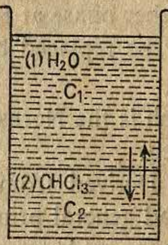


Fig. XV.1
Distribution of I_2 in H_2O and $CHCl_3$

An important limitation of the Distribution Law is that it is valid only when the molecular species of the solute is the same in the two phases. If the solute undergoes dissociation or association in any of the phases, the distribution Law (eqn. XV.1) as such will not hold good. Thus, if a solute remains unaltered in one solvent but undergoes partial dissociation in another, the ratio of the total concentrations (C_1/C_2) in the two phases will not be constant, but the ratio of the concentrations of the undissociated molecules in the two solvents would be fixed.

15.2. Thermodynamic basis of the Distribution Law

The Distribution Law can be derived from thermodynamic principles. Suppose in a system in equilibrium a component is present in two phases (1 and 2), having chemical potentials or molal free energies μ_1 and μ_2. Imagine a minute quantity ($\triangle n$ moles) of the component passes from phase 1 to phase 2 under conditions of equilibrium. Then from eqn. (XI.24), the net free energy change ($\triangle G$) would be,

$$\mu_1(-\triangle n) + \mu_2(\triangle n) = \triangle G$$

But under eqm. conditions, $\triangle G = 0$

Hence $$\mu_1(-\triangle n) + \mu_2(\triangle n) = 0$$

or $$\mu_1 = \mu_2 \qquad \text{...(XV.2)}$$

The chemical potential (or partial molal free energy) of a component in every phase must be the same under conditions of equilibrium.

But we have seen in Sec 11.7, eqn. (XI.29), that the chemical potential can be expressed in terms of activity (a), as, $\mu_i = \mu_i^0 + RT ln a_i$.

The equation (XV.2) will then take the form,

$$\mu_1^0 + RT\,ln\,a_1 = \mu_2^0 + RT\,ln\,a_2$$

where a_1, a_2 are the activities of the component in the two phases. μ_1^0, μ_2^0 are the standard chemical potentials of the component.

Then, at a constant temperature,

$$ln\frac{a_1}{a_2} = \frac{\mu_2^0 - \mu_1^0}{RT} = C\,\text{(constant)}$$

or $$\frac{a_1}{a_2} = \text{constant} \qquad \text{...(XV.3)}$$

That is, if the *activity of a component in one phase is fixed, its activity* in another phase at eqm. is also fixed. In ideal systems, say dilute solutions, activities may be replaced by concentrations C_1 and C_2. Then

$$C_1/C_2 = K$$

which is the Nernst Distribution Law. The Distribution Law is thus rigidly established.

Derived from theoretical considerations, the Distribution Law is thus a broad general principle, not confined to two liquid phases. The distribution of a component between any two phases will be governed by this law. When the solute is a gas and it is distributed between a liquid and a gas phase, we have seen that *Henery's Law* is applicable and $\frac{C_{gas}}{C_{liq}}$ = constant (eqn. XIII.21).

Henry's Law therefore is an illustration of the Distribution Law.

Limitations: The distribution law (C_1/C_2 = constant) is strictly valid when the concentrations are low, *i.e.* the solutions are dilute and behave ideally. Deviations are noticed when solutions have high concentrations.

If saturated solutions of the solute in the two solvents are brought together, then the ratio of their solubilities, would be expected to be equal to the partition coefficient

$$\frac{S_1}{S_2} = \frac{C_1}{C_2} = K\ \text{(Partition coefficient)}$$

But very often, S_1 and S_2 lead to quite concentrated solutions, in which there are interactions between the solute molecules and these are non-ideal. Hence S_1/S_2 is found to differ from the partition coefficient. Only if the solute be very sparingly soluble in both the solvents, then $S_1/S_2 = K$.

It should also be noted that the distribution law as such would not apply if the solute has any reaction with the solvent.

Moreover, it is known that addition of increasing amounts of solute sometimes influences the mutual miscibility of the two liquids very much. Sometimes with large concentrations of the solute, the mutual solubility of the two liquids increase and the concentrations of the solute tend to become the same in the two layers. In other cases, the mutual solubility of the liquids decrease in both the layers, or, it decreases in one layer and increases in the other. In such cases, the distribution law is not applicable.

15.3. Illustrations

Some examples of the application of the Distribution Law are given here.

(*a*) *Distribution of a solute with the same molecular species in both the solvents:* When iodine is distributed between water and carbon disulphide, there is no change in the molecular species of the solute in either solvent, hence $K = C_1/C_2$, which is confirmed from the experimental results given below:

TABLE: I_2 in CS_2 and H_2O (18°C); Conc (C) in gm/c.c.

I_2 in H_2O, C_1	4.1×10^{-4}	3.2×10^{-4}	1.6×10^{-4}	1.0×10^{-4}
I_2 in CS_2, C_2	0.174	0.129	0.066	0.041
$K = C_1/C_2$	420	400	410	410

Similar constancy of the ratio C_1/C_2 are found in many other cases, such as (i) boric acid in water and amyl alcohol (*ii*) $HgBr_2$ in water and benzene (*iii*) phenol in water and amyl alcohol (*iv*) H_2O_2 in water and ether (*v*) iodine in benzene and water, (*vi*) Br_2 in water and bromoform, etc.

(*b*) *Distribution of a solute which dissociates in one of the solvents and remains unchanged in the other:* Such a case is observed in the distribution of oxalic acid between the solvents water and ether. In the ether layer, the molecules of oxalic acid (H_2X) remains unchanged and suppose the concentration is C_1. In the aqueous layer, the concentration of the acid is C_2, but it is partly dissociated as,

$$\begin{array}{ccccc} H_2X & \rightleftharpoons & H^+ & + & HX^- \\ C_2(1-\alpha) & & \alpha C_2 & & \alpha C_2 \end{array}$$

where α is the extent of dissociation. $C_2(1-\alpha)$ is the concentration of the undissociated molecules in the aqueous layer.

In such a case, C_2/C_1, the ratio of the total concentrations in the two layer would not be constant but the ratio of the concentrations of the undissociated species would remain constant, *i.e.*

$$\frac{C_2(1-\alpha)}{C_1} = \text{constant} \qquad \ldots (XV.3)$$

The experimental results are given in the table here.

The value of α is ascertained from the dissociation constant (k_a) of the acid.

$$k_a = \frac{\alpha^2 C_2^2}{C_2(1-\alpha)} \approx \alpha^2 C_2^2\,; \quad \text{or} \quad \alpha = \sqrt{k_a}.C_2\,; \quad \text{since } \alpha \text{ is quite small.}$$

TABLE : DISTRIBUTION OF OXALIC ACID BETWEEN WATER AND ETHER (25°C)*

[$k_a = 5.36\times10^{-2}$, oxalic acid distributed between 50 c.c. water and 200 c.c. ether]

Initial conc. C	1.5	1.25	1.00	0.50	0.40
Conc. in aq. layer $C_2(1-\alpha)$	0.57	0.48	0.38	0.195	0.16
$K = \frac{C_2(1-\alpha)}{C_1}$	10.49	10.54	10.49	10.50	10.54

If the solute suffers dissociation in both the solvents with degrees of dissociation α_1 and α_2, then the partition coefficient would be,

$$K = \frac{C_1(1-\alpha_1)}{C_2(1-\alpha_2)}$$

(*c*) *Distribution of a solute when it associates in one of the phases.* When benzoic acid is added to a mixture of benzene and water, it suffers dimerisation in the benzene layer but in aqueous layer it remains unchanged (very small ionic dissociation being ignored). In the benzene layer, there is an equilibrium between dimers and the monomers, as, (z = benzoic acid)

$$Z_2 \rightleftharpoons 2Z$$

$$\text{Conc:} \qquad C_2(1-\beta) \quad 2\beta C_2$$

If C_2 be the total concentration of the acid in benzene layer and β be the degree to which dimers dissociate into single molecules, then

conc. of dimers $= C_2(1-\beta)$

and conc. of single molecules $= 2C_2\beta$

The eqm. constant is $K_1 = \dfrac{4\beta^2 C_2^2}{C_2(1-\beta)} \approx 4\beta^2 C_2$, (since β is very small)

$$\therefore \qquad \beta = \frac{\sqrt{K_1}}{2\sqrt{C_2}}$$

The conc. of single molecules in benzene layer $= 2\beta C_2 = \dfrac{2\sqrt{K_1}C_2}{2\sqrt{C_2}} = k_2\sqrt{C_2}$.

The distribution coefficient will be given by ratio of conc. of single molecules in the two layers

$$K = \frac{C_{\textit{in aqueous layer}}}{C_{\textit{in benzene layer}}} = \frac{C_1}{k_2\sqrt{C_2}}$$

or $\dfrac{C_1^2}{C_2}$ = constant, when C_1 = conc. in aqueous layer.

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* J. I. C. S. p 387, 6, 1955

The experimental values are given below for this system.

TABLE: DISTRIBUTION OF BENZOIC ACID BETWEEN WATER AND BENZENE AT 20°C

gm of acid per litre in water	*gm of acid per litre in benzene*	C_B/C_w	$\frac{C_B}{C_w^2} \times 10^{-3}$
2.89	97.0	33.6	13.9
1.95	41.2	21.6	13.4
0.97	10.5	10.8	13.6
0.79	7.3	9.4	14.0

To consider a general case where n molecules of solute associate in one phase, *i.e.*, $nA \rightleftharpoons A_n$. If C_2 be the conc. of the solute in solvent II which is practically wholly polymerised, and C_1 is conc. in solvent I, where it is present as single molecules, it can be shown in the same way,

$$C_1/\sqrt[n]{C_2} = \text{constant.} \qquad \ldots \text{(XV.4)}$$

In very dilute solutions, the ionic dissociation α in aqueous layer or the degree of dissociation β of dimers in benzene layer will have appreciable values. In such a condition, the distribution coefficient will be

$$K = \frac{[C_1(1-\alpha)]^2}{C_2\beta}$$

Many cases are known where the solute is associated in one solvent and dissociated in another. For example, picric acid is dissociated in water but remains as dimers in the layer of benzene. Lithium chloride distributed between water and amyl alochol, acetic acid or salicylic acid between water and chloroform, etc, are other examples.

15.4. Application of the Distribution Law

The distribution law is very helpful in the study of several physico-chemical problems.

(*a*) *Determination of mol. wt. of polymers:* The study of the concentration ratio of the solute in two solvents would reveal if any polymerisation of the solute occurs. If so, by using equation (XV.4), the value of n (the number of molecules associated) can be ascertained. The mol. wt. of the polymer is then evaluated.

(*b*) *Determination of Eqm. Constant:* The knowledge of distribution coeff. is also utilised in determining some eqm. constants, when one of the participants is soluble in two immiscible solvents. For example

$$KI + I_2 \rightleftharpoons KI_3 \quad ; \quad K_{eq} = C_{KI_3}/C_{KI}\cdot C_{I_2}$$

A solution of KI of known conc. (a) is taken in a stoppered bottle to which a small amount of iodine crystals are added. A portion of iodine combines with KI. To this is added some benzene and the bottle is shaken vigorously for several hours. A portion of iodine passes into the benzene layer. Let the partition coeff. of iodine between water and benzene be $P\,(= C_w/C_B)$.

The concentrations of iodine in the two layers are determined with thiosulphate titration.

Let b = Conc. of I_2 in benzene layer; then conc. of free I_2 in water layer is $b \times P$.

The concentration of I_2 estimated in water layer, C = Conc. of free I_2 + Conc. of KI_3.

∴ Conc. of KI_3 in water layer = $C - Pb$
And conc. of KI remaining = $a - c + Pb$

$$\therefore \qquad K_{eq} = C_{KI_3}/C_{I_2}.C_{KI} = \frac{C-Pb}{Pb(a-c+Pb)}$$

The eqm. const is thus known.

The hydrolysis-constant (say of aniline hydrochloride), the composition of complexes etc. are also determined in a similar way.

(c) *Extraction of a component from the solution of mixtures:* If a desired component be present along with other substances in solution, an immiscible solvent in which the component is highly soluble is added and shaken. The component then distributes itself between the two immiscible liquids, the major portion passes over to the added solvent. Thus, it is extracted out free from other contaminating materials. In the qualitative analysis of iodides and bromides, the halogen is set free in aqueous medium and the solution is shaken with $CHCl_3$ or CS_2, when the halogen mostly passes into the organic solvent and identified.

This principle is also employed in the **Parke's Process** of extraction of silver from argentiferrous lead. To the molten lead is added molten zinc in which silver is 300 times more soluble than in lead. On stirring, silver passes into the molten zinc which is very slightly miscible with molten lead. The zinc layer is separated and zinc is distilled off leaving behind silver.

Organic compounds are almost always separated by such solvent extraction method.

15.5. Solvent Extraction

Organic compounds are generally much more soluble in organic solvents like benzene, chloroform, ether, etc. than in water and these solvents are immiscible with water. Organic compounds are then easily separated from mixture with inorganic substances in aqueous medium by adding benzene, chloroform, etc. On shaking, these separate into two layers. Since organic compounds have their distribution ratio largely in favour organic solvents, most of them passes into the non-aqueous layer. Finally this non-aqueous layer is removed and distilled to obtain the purified compound.

In such solvent extraction it is advantageous to use a given volume of the extracting solvent in small lots in successive stages than the whole quantity at a time. Suppose a solute A is present in 100 c.c. water and that 100 c.c. of ether will be used for its extraction and suppose that the distribution coefficient of A between ether and water is 4.

$$i.e., \text{ partition coefficient, } K = \frac{\text{Conc. of } A \text{ in ether}}{\text{Conc. of } A \text{ in water}} = 4$$

(*i*) When the whole of 100 c.c. ether is used at a time for extraction, suppose w_ϵ gram of solute pass into ether layer and w_w gram left in aqueous layer, so that

$$\frac{w_\epsilon/100}{w_\omega/100} = 4, \quad i.e., \frac{w_\epsilon}{w_\omega} = 4 \quad \text{or} \quad \frac{w_\epsilon}{w_\epsilon + w_\omega} = \frac{4}{5}$$

This means that 100 c.c. ether has separated 4/5th or 80% of the solute originally present.

(*ii*) Now let us use 100 c.c. of ether in two successive extractions, using 50 c.c. each time. Then in the first stage,

$$\frac{w_\epsilon/50}{w_\omega/100} = 4, \quad \text{or} \quad \frac{w_\epsilon}{w_\omega} = 2, \quad \text{or} \quad \frac{w_\epsilon}{w_\epsilon + w_\omega} = \frac{2}{3}$$

That is, in the first extraction 2/3rd *i.e.*, 66.7% is extracted, Hence 1/3rd of the original amount is still retained in aqueous medium. In the second extraction using again 50 c.c. ether, we shall further extract 2/3rd of 1/3rd *i.e.*, 2/9the of the original amount. In other words, in two extractions using the same 100 c.c. ether, we can separate ($\frac{2}{3}+\frac{2}{9}$) or $\frac{8}{9}$ *i.e.*, 88.9% of the original amount of the solute. Thus a two-stage extraction is more efficient. If the same 100 c.c. solvent were used in four or five lots, a still greater proportion could be extracted.

A generalised formula can be easily suggested for the amount remaining unextracted after a given number of operations. Let V c.c. of a solution containing x_0 gm of substance be extracted with L c.c. of a solvent. Let x_1 gm of substance remain unextracted in water layer. Then,

$$\text{conc. of the substance in solvent} = \frac{x_0 - x_1}{L}; \text{ and in water} = \frac{x_1}{V}$$

$$\therefore \quad \text{Distribution coefficient, } K = \frac{\dfrac{x_1}{V}}{\dfrac{x_0 - x_1}{L}}$$

$$\text{or} \qquad x_1 = \frac{KV(x_0 - x_1)}{L} = x_0 \frac{KV}{KV + L}$$

If second extraction again with L c.c. solvent is made, the quantity unextracted would be

$$x_2 = x_1 \frac{KV}{KV+L} = x_0 \frac{KV}{KV+L} \cdot \frac{KV}{KV+L} = x_0 \left(\frac{KV}{KV+L}\right)^2$$

Similarly after *n*-th extraction, the quantity left behind would be

$$x_n = x_0 \left(\frac{KV}{KV+L}\right)^n \qquad \ldots (A)$$

If the entire quantity of the extracting solvent be used in one lot, then unextracted,

$$x' = x_0 \left[\frac{KV}{KV+nL}\right] \qquad \ldots (B)$$

Since the quantity within the parantheses is less than unity, (*A*) is smaller than (*B*) and x_n will be smaller the greater the value of *n*. Hence it is more economical to use the solvent in portions,

15.6. Calculations

Example 1. At 20°C, the quantities of succinic acid between 20 c.c. water and 20 c.c. ether are 0.15 gm and 0.027 gm. Calculate the conc. of succinic acid in the ether layer which is in eqm. with 0.05 gm of it in 20 c.c. water.

$$\text{Partition coefficient, } K = \frac{C_{\text{water}}}{C_{\text{ether}}} = \frac{0.15/20}{0.027/20} = 5.55$$

In the given system, let the concentration of succinic acid in the ether layer be x gm per 20 c.c. The conc. in aqueous layer is 0.05 gm per 20 c.c. Then

$$\text{Distribution coefficient, } K = \frac{0.05/20}{x/20} = 5.55$$

or

$$x = \frac{0.05}{5.55} = 9 \times 10^{-3}\ \text{gm/20c.c.}$$

$$= 0.45\ \text{gm per litre}$$

Example 2. 50 c.c. of an aqueous solution of iodine containing 4 mg of iodine is shaken with 10 c.c. of CCl_4 and the mixture is allowed to separate. Given that iodine is 85 times more soluble in CCl_4 than in water, calculate the quantity of iodine left behind in the aqueous layer. (Delhi Univ.)

Suppose x mg iodine passes into the CCl_4 layer. Conc. in CCl_4 layer per c.c. $= x/10$ mg, conc. in aq. layer $= (4-x)/50$ mg

$$\therefore \qquad \frac{x/10}{(4-x)/50} = 85$$

whence $x = 68/18$. So the quantity left in water is

$$4-x = 4-(68/18) = 0.222\ \text{mg.}$$

[The same result would come out if molar conc. be used]

Example 3. The molar concentrations of acetic acid distributed between water and CCl_4 are as follows:

Aqueous layer (C_1)	5.02	7.98	10.70
CCl_4 layer (C_2)	0.292	0.725	1.31

Show that in CCl_4-layer, acetic acid exists as dimers.

If acetic acid be present as dimers in the non-aqueous layer, then

$$\frac{C_1^2(\text{aq.})}{C_2} = \text{constant}$$

Substituting the values given

$$(a)\ \frac{5.02^2}{0.292} = 86.3 \qquad (b)\ \frac{7.98^2}{0.725} = 88.2 \qquad (c)\ \frac{10.70^2}{1.31} = 87.3$$

The near constancy of C_1^2/C_2 confirms that acetic acid is present as dimers in CCl_4-layer

Example 4. The distribution coefficient of an alkaloid between chloroform and water is 20. Compare the weights of the alkaloid remaining in aqueous solution after 100 c.c. of it containing 1 gm is shaken with (*a*) 100 c.c. chloroform and (*b*) with two successive quantities of 50 c.c. chloroform.

$$\text{Distribution coeff., } K = \frac{C_{\text{water}}}{C_{CHCl_3}} = \frac{1}{20}$$

(*i*) when 100 c.c. $CHCl_3$ is used in 1 lot, the amount unextracted,

$$x_u = x_0\left(\frac{KV}{KV+L}\right) = 1\left(\frac{\frac{1}{20}\times 100}{\frac{1}{20}\times 100+100}\right) = 0.0476 \text{ gm}$$

(*ii*) when 50 c.c. $CHCl_3$ is used in 2 lots, the amount unextracted,

$$x'_u = x_0\left(\frac{KV}{KV+L}\right)^2 = 1\left(\frac{\frac{1}{20}\times 100}{\frac{1}{20}\times 100+50}\right)^2 = 0.0083 \text{ gm}$$

Example 5. An organic compound is extracted from 500 c.c. aqueous solution with successive quantities of 25 c.c. $CHCl_3$. Calculate the number of extractions needed for 95% recovery of the organic compound. Given partition coefficient, $C_{CHCl_3}/C_{H_2O} = 20$.

The amount left behind is 5%. Suppose *n* extractions are necessary. Then

$$\frac{5}{100} = \left(\frac{KV}{KV+L}\right)^n = \left(\frac{\frac{1}{20}\times 500}{\frac{1}{20}\times 500+25}\right)^n = (\tfrac{1}{2})^n$$

or $$n = \frac{\log 5/100}{\log \frac{1}{2}} = 4.3$$

Hence to obtain 95% extraction, 5 successive extractions will be needed.

EXERCISES

1. State and explain the Distribution Law. Discuss its limitations.

Iodine is distributed between CCl_4 and water. Their amounts in 50 c.c. of each solvent are found as follows:

CCl_4—layer	11.18	7.6	6.12	3.06
Water—layer	0.13	0.089	0.072	0.036

Show that the results support the Distribution Law.

2. How is the distribution method adopted to show that benzoic acid is associated in benzene? (Madras Univ.)

Solution of a weak organic acid in benzene was shaken with water. At eqm., the following results were obtained for the concentration (C_1) in benzene layer and (C_2) in water layer

C_1	2.66	6.35	9.70
C_2	1.65	2.54	2.89

Show that in benzene the acid exists as double molecules. (Kerala Univ.)

3. How can experimental study of the distribution of a substance between two immiscible liquids decide whether it is associated or dissociated in one of the liquids and to what extent? (Delhi Univ.)

Benzoic acid distributes itself between water and benzene in such a way that in a definite volume of water there are 1.50, 1.95 and 2.97 g benzoic acid while in an equal volume of benzene there are 24.2, 41.2 and 97.0 g benzoic acid. What conclusion can be drawn from these results concerning the molecular condition of benzoic acid in benzene? (Guru Nanak Univ.)

[Ans. dimers]

4. Calculate how much succinic acid would be extracted from 100 c.c. water containing 5 gm succinic acid if extracted with 50 c.c. ether. The partition coeff. $C_{water}/C_{ether} = 5.5$. [Ans. 0.417] (Bombay Univ.)

5. Calculate the percentages of the solute which would be extracted from 100 c.c. of aqueous solution by using 100 c.c. ether (*i*) in two equal instalments and (*ii*) in one lot of 100 c.c. The partition Coeff. $C_{\text{ether}}/C_{\text{water}} = 5.0$ [Ans. (*i*) 91.8% (*ii*) 83.3%]

6. An aqueous solution contains 16.0 gm of a substance per litre, When one litre of the solution is treated with 100 c.c. ether, 12.0 gm of the substance is extracted from the aq. solution. How much of it would be extracted by a further 100 c.c. of ether, the molecular state is the same in both solvents. (Delhi Univ.) [Ans. 3 gm]

7. The Distribution coefficient of iodine between water and CS_2 is 1.7×10^{-3}. One litre of aqueous solution containing 1 gm iodine is shaken with 50 c.c. CS_2. What will be the residual amount of iodine in water? If 50 c.c. of CS_2 were used in five succescive steps of 10 c.c. each, what would be the amount of iodine left in water? [Ans. 2.97×10^{-2} gm; 6.5×10^{-5} gm]

8. A valuable organic substance is to be extracted to an extent of 99.9% from v volume of an aqueous solution. The volume of the extracting solvent each time has also the volume v. How many extractions would be required if distribution coefficient, $K = C_{\text{solvent}}/C_{\text{water}} = 10$. [Ans. $n = 3$]

CHAPTER 16

HETEROGENEOUS EQUILIBRIUM : THE PHASE RULE

16.1. The Heterogeneous Systems

When a system consists of parts which have different physical properties (and often also different chemical properties) and which are separated by boundary surfaces, the system is said to be a heterogeneous one. In such a system, the concentrations (and often compositions) in different parts would be different. When due to a physical or chemical process, there is movement of one or more constituents from one state of aggregation to another, *i.e.* from one phase to another, the equilibrium finally attained is a heterogeneous one. In the foregoing pages, some types of heterogeneous equilibria have already been discussed. It has been shown that the heterogeneous processes of vaporisation, condensation, sublimation, transition of one solid into another follow quantitatively Clausius Clapeyron equation, Raoult's Law, etc. The solubilities of solids, liquids and gases have been thoroughly considered in chapter 14. The distribution of a solute in different phases obeys Nernst Distribution Law (Chap. 15). These are all heterogeneous systems in equilibrium. In the quantitative study of heterogeneous systems involving chemical reactions, the application of the Law of mass action is inescapable as shown in page 183.

In 1876 Willard Gibbs enunciated, from thermodynamic considerations, a brilliant and yet simple principle called the *Phase Rule*, which would furnish information regarding the physical equilibria of any heterogeneous system and the behaviour of such systems under changing experimental conditions.

16.2. Definitions

Before discussing the Phase Rule, it would be convenient to be conversant with the meaning and significance of at least three terms which are often used in the study of heterogeneous systems. These terms are *Phases*, *Components* and *Degrees of Freedom*. It will be seen that there is a specific relation between these in the Phase Rule.

Phases : A *phase is defined as a physically distinct but homogeneous part of a system separated from other parts by boundary surface.* A heterogeneous system is therefore composed of two or more phases. Thus a system containing water and its vapour has two phases—the liquid phase and the vapour phase; each phase is homogeneous and distinct and there is the surface-boundary between the two. A gas mixture is always a single phase. Similarly, all homogeneous solutions are one-phase systems, whatever may be the number of substances present in the same. Every solid, however, constitutes a separate phase. So, when calcium carbonate dissociates into calcium oxide and carbon dioxide, there are two solid phases—viz. calcium carbonate and calcium oxide—and one gas phase of carbon dioxide. That is, it is a three-phase heterogeneous system.

Components : *The minimum number of independent chemical constituents by which the composition of every phase of the system can be expressed determines the number of components.* It must be clearly understood that the components of a system are not synonymous with the consitutuents of the system. All the constituents need not be components, but all the components must be included in the constituents.

To illustrate: The system water-water vapour contains only one component. Both the phases may be expressed by one chemical individual namely, H_2O. It is a one-component system. A cane-sugar solution will be a two-component system as there are two independent chemical substances which determine the composition of the solution, namely, H_2O and $C_{12}H_{22}O_{11}$ (cane sugar). Again, ferric chlordie and water can give rise to solids like $Fe_2Cl_6.12H_2O$, $Fe_2Cl_6.7H_2O$,$Fe_2Cl_6.5H_2O$, $Fe_2Cl_6.4H_2O$ and anhydrous Fe_2Cl_6, as also the solution, ice and the vapour phase. But to express the composition of any phase, two chemical individuals—H_2O and Fe_2Cl_6—are only required, It is thus a two-component system.

If a system contains calcium carbonate at a higher temperature, three substances are likely to be present in the system viz, calcium carbonate, calcium oxide and carbon dioxide.

$$CaCO_3 = CaO + CO_2$$

There is however a restriction that the amount of CaO and CO_2 must be equivalent. As such, the composition of any phase can be represented by the concentrations of any two of the three individuals; say, CaO and CO_2. The phase calcium carbonate is lCaO + $l$$CO_2$; the phase calcium oxide is mCaO + 0CO_2; and the gas phase carbon dioxide is $m$$CO_2$ + 0CaO. Hence, although three constituents occur in the system, it is really a two-component system.

Degrees of Freedom : *The number of degrees of freedom is the number of variables which must be specified in order to define the system completely.*

Alternatively, it is also defined as, *the number of degrees of freedom of a system is the number of factors* (*temperature, pressure, concentrations, etc.*) *which can be varied independently without altering the number of phases.* It means that if the state of a system depends on F independent variables, its degree of freedom is F. It is illustrated with an example.

Suppose a gas is enclosed in a cylinder with a movable piston as in Fig. XVI.1-I. It is a one-phase system. Let the volume of the gas be intentionally kept constant, we can now alter the temperature and pressure without altering the number of phases. Instead, if the temperature be fixed, the other two factors pressure and volume can be varied and therefore the state of the system remains undefined. But if we fix two of the factors—say, temperature and pressure—then the third (volume) is definite. So, by fixing two variable factors, the system is completely defined. Such a system in which two factors can be independently varied without changing the number of phases has two degrees of freedom or it is a *bi-variant* system.

Again, suppose a liquid is in contact with its vapour as in Fig. XVI.1-II. In this case if we fix either the temperature or the pressure, the system is defined completely, subject to the condition of the co-existence of both the phases. For any given temperature, the vapour pressure is immediately fixed. If at a fixed temperature, pressure is altered, one of the phases would disappear. So, this is a system with one independent variable factor or it is a *univariant* system possessing one degree of freedom.

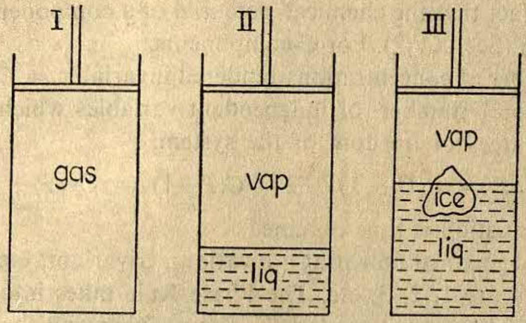


Fig. XVI. 1

Further, suppose the system in Fig. XVI.I-III contains a substance in equilibrium in three phases—say, ice, liquid water and water vapour. This is possible at a particular pressure and temperature. If we vary any one of these factors, either pressure or temperature, one of the phases would disappear. If we lower the temperature, all liquid will solidify and if we raise the temperature the ice will disappear. Hence in this case there is no independent variable or it is a non-variant system, the number of degrees of freedom being zero.

16.3. The Phase Rule

The Phase Rule presents a relation between the components, phases and the degrees of freedom of a heterogeneous system. If a system containing C components has P coexisting phases, the degree of freedom F is given by

$$F = C - P + 2$$

This is the Phase Rule.

It is concerned with effects which changes in pressure, temperature and concentrations will have on the eqiulibrium of any heterogeneous system. The beauty of the Phase Rule lies in its extraordinary simplicity and the capacity of bringing within its ambit most widely divergent and unrelated heterogeneous equilibria.

An elementary derivation of the Phase Rule may be made in the following way. To know or define a system completely, it is necessary to ascertain all the parameters or variables of the system, namely, the pressure, the temperature and the concentrations of the components in all the phases.

Let a given system have

number of components $= C$, and the number of phases $= P$

For any one phase, the concentrations of $(C-1)$ components have to be specified; the concentration of the remaining component is obtained by difference. For P number of phases, the total of concentration variables to be specified would be $P(C-1)$. Two other parameters which are also to be known are pressure and temperature.

So, the total number of variables required to be specified to define the system $= P(C-1)+2$

But if the concentration (or activity) of a component is specified in one phase, its concentration in all the other (P—1) phases would be fixed and unalterable. This is due to the fact that the chemical potential of a component in all the phases in eqm. is the same (See. XV.2). For C-components,

the number of concentrations rendered invariable $= C(P-1)$

Hence, the total number of independent variables which would define the system, *i.e.* the degrees of freedom of the system,

$$F = P(C-1)+2-C(P-1) = C-P+2$$

The Phase Rule equation is thus obtained.

The systems are named univariant, bivariant, trivariant, etc. according as the degrees of freedom are 1, 2, 3, etc. The Phase Rule takes into account only the variables of temperature, pressure and the composition and the influence of other factors such as electric, magnetic, gravitational, surface forces, etc. is ignored. The equation does not depend upon the nature or the amount of the substances. It also does not assume anything regarding the constitution of the matter or the molecular complexity. The Phase Rule tells us that the systems having the same degrees of freedom shall behave in a similar fashion. It thus enables us to classify the states of equilibrium. It is immaterial whether the phase-changes in systems are chemical or physical, if the number of degrees of freedom be the same, the systems shall behave similarly when temperature, pressure and composition (concentrations) are varied.

To illustrate: We may take the following three different systems, namely, (*i*) Water and its vapour (*ii*) Solid β-tin and its vapour and (*iii*) Solid calcium carbonate in contact with its dissociated products calcium oxide and carbon dioxide. The last system involves a chemical reaction while the other two are physical changes. The details of the systems are:

System	Co-existing phases	Number of phases and components	Degrees of freedom
Water and vapour	liquid-gas	$P = 2, \ C = 1$	$F = 1-2+2 = 1$
Tin and its vapour	solid-gas	$P = 2, \ C = 1$	$F = 1-2+2 = 1$
Calcium carbonate	solid-gas	$P = 3, \ C = 2$	$F = 2-3+2 = 1$

We have already seen previously that the number of components in the system in which calcium carbonate is dissociated is two.

Now all the systems, in accordance with the Phase Rule, are univariant and hence all of them are expected to behave similarly. The experimentally observed variation of vapour pressures with temperature for the three systems are given in Figs. XVI.2 (*a*, *b*, *c*).

The similarity of curves indicates that although the systems are widely different yet they behave in a like manner. Alternatively from a knowledge of the degrees of freedom and the number of components, it is possible to predict the number of phases coexisting in the system in eqm. With the help of the Phase Rule, we group together widely different phenomena and it guides us to ascertain the existence of a new phase. The Phase Rule has been of great value in the practical field, especially in industries, such as in the isolation of salts from mixtures, preparation of alloys, etc. It helps in the adjustment of temperature, composition, etc. to obtain a desired product. The separation of potassium chloride from stassfurt deposits is an outstanding example.

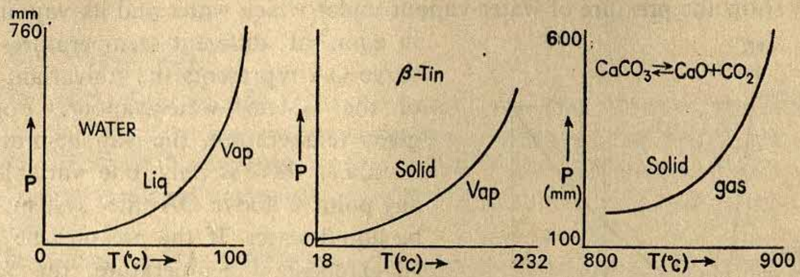


Fig. XVI.2(*a*) Water and its vapour (*b*) Tin and vapour (*c*) Dissociation of $CaCO_3$

Phase Diagrams: The conditions under which different phases would coexist in a heterogeneous system are conveniently described graphically by plotting two or more of the parameters or variables ($T, P, C_1, C_2, \ldots$) as in Fig. XVI.2. These are called 'phase diagrams'. With two variables, rectangular co-ordinates are used, but when three variables are concerned, solid diagrams are needed. With such diagrams, the Phase Rule easily interprets the equilibrium conditions of the system. The study of the application of Phase Rule has been, for convenience, classified according to the number of components present, such as one-component system, two component system, etc.

ONE COMPONENT SYSTEMS

16.4. The System, H_2O

One component systems shall comprise of a pure substance only. The simplest and a typical example is the system containing H_2O, which under ordinary circumstances can have three possible phases—ice, water and water-vapour.

(*a*) If the system consists of only one phase, say vapour, then

$$F = C - P + 2 = 1 - 1 + 2 = 2,$$

i. e. the system would be bivariant. That is, both pressure and temperature can be varied simultaneously without any phase-change, or, both pressure and temperature variables must be determined to define the system.

(*b*) If the system contains two phases in eqm., say water and vapour, or say ice and water, then

$$F = C - P + 2 = 1 - 2 + 2 = 1,$$

i.e., the system would be *univariant*. The eqm. between the two phases would be known if only the temperature or the pressure be fixed.

The truth of the above predictions of the Phase Rule is borne out by the phase diagram of water as in Fig. XVI.3. The line OA is the vapour-pressure curve for water, the vapour-pressure increasing with rise in temperature. The points on OA show the pressure of water-vapour under which water and its vapour exist in eqm. at different temperatures. The curve OA represents the univariant states of the system—water/vapour. For any given temperature, the vapour-pressure is fixed, *i.e.*, there is only one variable. For any point *x* above OA the system would be liquid water. If the pressure be lowered at constant temperature, the vapour-phase would appear at *y*. On further lowering of pressure to *Z*, the system would be completely vapour (temperature remaining constant). Hence OA in the phase diagram is the boundary line between the two phases, water and its vapour.

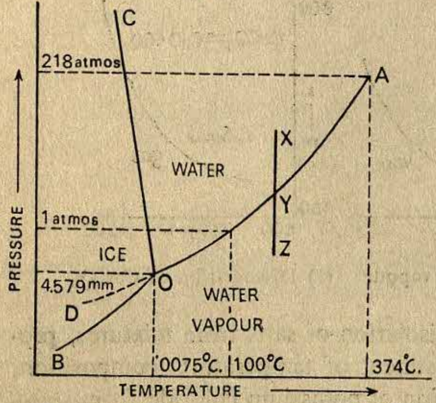


Fig. XVI.3. The phase-diagram for water (not to scale)

There is however an upper limit for OA, terminating at A, its critical state ($P = 218$ atm, $t = 374°C$), when liquid phase is no longer distinguishable from vapour phase.

Similarly the curve OB denotes the vapour-pressure curve of ice, or more appropriately, the sublimation pressure—temperature curve for ice. It registers the vapour pressures under which ice is in eqm. with its vapour at different temperatures. This is also the boundary line between ice and vapour. The slope of OB is less than that of OA, *i.e.* OA and OB are not continuous.

On the other hand, OC is the freezing point curve indicating the equilibria at different temperatures between water and ice. The line has a negative slope, which means that the melting point is lowered with increase in pressure.

Each of the three lines (OA, OB, OC) indicates the two-phase equilibria and represents univariant states. The areas enclosed between these lines represent regions of a single phase, *i.e.*, bivariant states of the system. Thus, the region AOB is vapour, BOC ice and COA water.

The point O where the three lines meet, all the three phases should co-exist. This is called a **triple point.** The pressure at this point has been found to be 4.58 mm. The f. pt. of water is 0°C under 760 mm, hence by Clapeyron equation, the f. pt under 4.58 mm would be + .0075°C.

So at triple point of water, $P = 4.58$ mm and $t = +\ .0075°C$. There are three phases, hence at the triple pt., $F = 1 - 3 + 2 = 0$. The system is non-variant at the triple point. If either the temperature or the pressure be changed, one of the phases would disappear.

It is possible to cool water below its f. pt. without solidification, water is then present in *supercooled state.* The supercooled state is unstable and is usually described as a *metastable state* The vapour-pressure curve of supercooled water is given by OD (the dotted line), which is a continuation of AO. The line OD is above OB, the vapour-pressure curve of ice. This shows that the *vapour-pressure of the metastable phase is higher than that of the stable phase*, which is a general principle.

16.5. The System CO_2

The phase diagram of CO_2 is quite similar to that of water, as shown in Fig. XVI.4. OA is the eqm. vapour-pressure-temperature curve of liquid carbon dioxide. OB is the f. pt. curve of liquid CO_2 under different pressures and OC is the vapour-pressure curve of solid CO_2. The curve OB has a positive slope (cf. H_2O system).

The points on OA, OB, OC stand for co-existence of two phases liquid-gas, solid-liquid and solid-gas. Hence these lines represent univariant systems. The areas AOB, BOC, COA indicate the existence of one phase only, namely liquid, solid and gas respectively. The areas are bivariant, *i.e.* both pressure and temperature have to be determined to describe the state.

The curve OA has its upper limit at its critical point, $p_c = 73$ atm; $t_c = 31.2$°C.

The triple point O, where the three phases can co-exist, is as usual non-variant, and the co-ordinates are $p = 5.11$ atm and $t = -56.6$;C. A glance at the diagram will reveal that liquid carbon dioxide cannot exist at any pressure below 5 atmospheres. This has a far-reaching consequence. Suppose we have solid CO_2 at atmospheric pressure at very low temperature as at 'a'. If now, at const. pressure the temperature is raised gradually, the solid will change from 'a' to 'b' where it would be a gas, without melting *i.e.*, without passing through the liquid state. In other words, *sublimation* would occur.

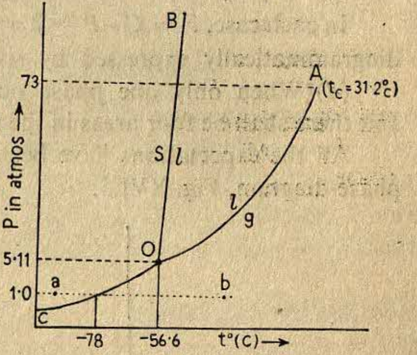


Fig. XVI.4. The phase diagram for CO_2 (not to scale)

The vapour pressure exerted by a solid is usually small. In some solids such as naphthalene, camphor, iodine, etc. the vapour pressure even at ordinary temperature is appreciable and it rises with increase in temperature. If the vapour pressure of a solid reaches the atmospheric pressure before the solid reaches its melting pt. the solid will then vaporise away before melting or sublimation would occur. In other words such solids would be found to sublime. Generally speaking, when the triple-point pressure is higher than the external pressure on the system, then the vapour pressure of the solid reaches the external pressure before the solid melts and consequently sublimation occurs.

16.6. The System, Sulphur

We may next consider the phase diagram of sulphur which is somewhat complicated due to its polymorphic nature. Sulphur does occur in different forms, some of which are unstable or metastable. Broadly we recognise four phases of sulphur, namely (*a*) Rhombic sulphur (S_α), (*b*) Monoclinic sulphur (S_β), (*c*) liquid sulphur and (*d*) sulphur vapour.

With these four phases of sulphur, the Phase rule would lead to the following predictions as to the possible systems that would be in equilibrium.

(*a*) A system with all the four phases cannot exist. For in that case,

$$F = C - P + 2 = 1 - 4 + 2 = -1,$$

the degree of freedom becomes negative, which has no meaning.

(*b*) There are four possibilities of three phases out of four co-existing at eqm., which are

(*i*) $S_\alpha - S_\beta -$liq (*ii*) $S_\alpha - S_\beta -$vapour (*iii*) $S_\alpha -$liq$-$vapour (*iv*) $S_\beta -$liq$-$vapour

For each of these systems, $F = C - P + 2 = 1 - 3 + 2 = 0$

i.e., non-variant, in which all parameters are fixed. Hence such systems are represented by points. Four such triple points are thus expected.

(*c*) Six possible systems of two-phases are realisable, namely

(*i*) $S_\alpha - S_\beta$	(*ii*) $S_\alpha -$liq.	(*iii*) $S_\alpha -$vapour
(*iv*) $S_\beta -$liq.	(*v*) S_β $-$vap.	(*vi*) liquid—vapour.

In each case, $F = C - P + 2 = 1 - 2 + 2 = 1$, the system would be univariant, diagrammatically expressed by six lines.

(*d*) When only one phase occurs, the system would be bivariant, $F = 2$, and there shall be four areas in the phase diagram to represent the four phases.

All the expectations have been experimentally realised and are shown in the phase-diagram, Fig. XVI.5.

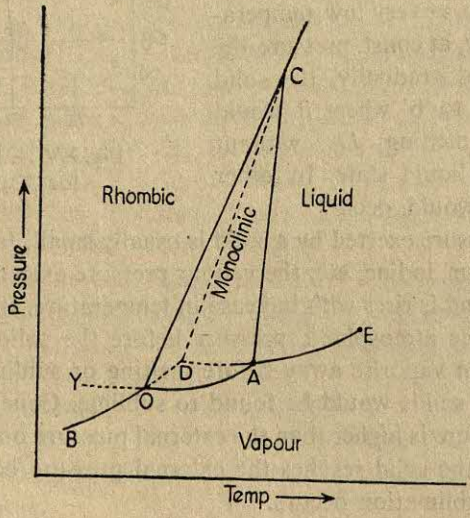


Fig. XVI.5. Phase diagram of sulphur (not to scale)

Co-ordinates:		*A*	*O*	*C*	*D*
	P	0.025 mm	0.01 mm	1290 atm	0.03 mm
	t°(C)	120°	95.5°	151°	114°

The curve BO shows the change of vapour-pressure of rhombic sulphur with change in temperature. The curve OA shows the vapour-pressure of monoclinic sulphur at different temperatures. These two curves intersect at O where $t = 95.5°C$. At Q, the three phases rhombic, monoclinic solids and the vapour can exist in equilibrium with one another and this is a triple point for these three phases. This point is also known as the *transition temperature* for the two solid phases $S_\alpha \rightleftharpoons S_\beta$. If S_α be rapidly heated beyond 95.5°C without permitting sufficient time for transformation into S_β, the rhombic sulphur will remain in metastable state and the vapour pressure will change along OD, which is above the curve for stable state OA. With time S_α will change into S_β. Similarly if S_β is cooled below 95.5°C. its vapour pressure will change along OY. S_β is metastable below 95.5°C and will slowly change into S_α. Above the transition temperature one form is stable and below the transition temperature the other form.

The upper limit of the vapour pressure curve of monoclinic sulphur is A, where it melts into liquid sulphur ($p = 0.025$ mm) at 120°C and AE is the vapour pressure curve of liquid sulphur. Since OA and AE intersect at A, the three phases S_β, liquid and vapour can exist in equilibrium at this point. That is, A is a triple point for S_β-liq-vapour.

Again, the change in melting point of monoclinic sulphur into liquid with increase in pressure, governed by Clapeyron relation, is represented by AC. At any point on this line AC, monoclinic and liquid sulphur are in equilibrium forming univariant systems. This is identical to ice-water equilibrium.

Similarly the curve OC indicates the changes in transition temperature of $S_\alpha \rightleftharpoons S_\beta$ with increase in pressure. Every point on this line indicates a univariant system of two solid phases S_α and S_β. The transition of rhombic to monoclinic sulphur is accompanied by an increase in volume, $\Delta v = 0.01395$ c.c./gm. Hence, from Clapeyron equation, transition point is increased by increase of pressure, $\Delta T = 0.04°$/atmosphere.

At C, where AC and OC intersect, we have a third triple point. At this point S_α, S_β and liquid sulphur can remain in equilibrium with one another, ($p = 1290$ atm, $t = 151°C$). Beyond this point, the monoclinic sulphur cannot exist. The occurrence of monoclinic sulphur is thus restricted within the region AOC.

Liquid sulphur when supercooled has a vapour pressure curve (for such metastable condition) along AD, a continuation of EA. The vapour-pressure curve of metastable S_α is OD. These two intersect at D, ($t = 114°C$) where sulphur vapour, liquid sulphur and rhombic sulphur would co-exist. This is the fourth triple point, S_α-liq-vapour. The line DC represents the change of freezing temperature of liquid to rhombic sulphur with increase in pressure. The point D is indeed a metastable triple-point and can be experimentally realised only under carefully manipulated conditions.

There are thus four triple points at O, A, C and at D. The lines representing univariant two-phase systems are BO (S_α/vap), OA (S_β/vap), AE (liq/vap), AC (S_β/liq), OC (S_α/S_β), DC (S_α/liq).

These six lines have divided the whole diagram into four regions of bivariant systems containing a single phase: areas BOAE (vapour), CAE (liquid), COA (S_β), BOC (S_a). The phase diagram thus completely represents the behaviour of sulphur under any given condition of temperature and pressure.

TWO COMPONENT SYSTEMS

The two component systems occur in innumerable types. The equilibria of some two component systems, such as binary liquid mixtures and liquid-vapour systems, have already been studied earlier (chap XIII). In this chapter we shall discuss from the stand-point of the Phase Rule some simple two component systems involving solid-liquid and solid-gas phases. Of the solid-liquid systems, the eutectic systems are the simplest. The solid-liquid systems of the following three types are considered here. The two components are completely miscible in the liquid phase.

Type I—Pure components separate from the liquid phase.

Type II—Solid compound of the components with *congruent m. pt* separates from the liquid phase.

Type III—Solid compound of the components with *incongruent m. pt.* separates from the liquid phase.

The metal alloys and salt hydrates come within this category.

When the two components are present only in one phase ($P = 1$), then $F = C - P + 2 = 2 - 1 + 2 = 3$. This means that the three variables,—pressure, temperature and the concentration of a component—have to be specified to describe the system. The phase diagram with three variables, can be plotted with a set of three co-ordinate axes at right angles to each other. Usually, the studies of most of the systems are carried out in open vessels and the pressure is always one atmosphere. In other words, the pressure variable is ignored.

Since one variable is not taken into consideration, the phase rule is modified as $F = C - P + 1$

Most commonly, phase diagrams in such systems are made by plotting composition vs. temperature. We may now take some examples of the types mentioned above.

16.7. Simple Eutectic Systems

The Fig. XVI.6 represents the phase diagram of such a eutectic system in which the two components *A* and *B* are completely miscible in liquid state and pure components only crystallise from solution. In this diagram A and B are the freezing points of pure components *A* and *B*. The addition of component *B* to *A* will cause the freezing point to be lowered. The points on AE denotes the concentrations of solutions saturated with *A* at different temperatures between A and T_E, *i.e.*, AE is the freezing points of solutions which yield *A* as a solid phase. Similarly the curve BE denotes the freezing points of solutions which yield B as a solid phase from the solutions (between the temperatures B and T_E). At *E*, the point of intersection of the two curves, the solution is saturated with both *A* and *B*. Hence at E, three phases co-exist, namely, solution, solid *A* and solid *B*.

Therefore at E, $F = C - P + 1 = 2 - 3 + 1 = 0$, the system is non-variant, Both temperature and composition are fixed. This means if either the temperature or the composition is altered, one of the phases will disappear. If the temperature is lowered, the saturated solution will disappear and the whole mass will solidify as a mixture of pure *A* and pure *B* crystals. If the temperature is raised, the solids will melt. The temperature at E, *i.e.*, T_E is the lowest temperature at which a liquid phase may exist in the system. The point E is called the **eutectic point,** the composition L is the *eutectic composition* and T_E the *eutectic temperature* of the system. The eutectic mixture has a definite composition (L) and definite melting point (T_E), yet it is not to be regarded as a compound for, (*i*) the components are not in stoichiometric proportion and (*ii*) the mixtures reveal the existence of separate crystals under a microscope.

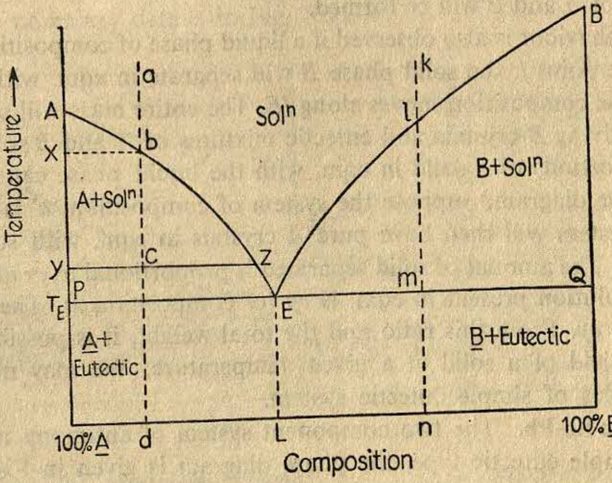


Fig. XVI.6. Simple eutectic diagram

Along the line AE, crystals of *A* separate from the solution. The points on this line indicate the 'beginning of freezing' and is the **liquidus.** Likewise the line BE is the other liquidus which represents the beginning of freezing of *B* from the solution. The system has thus the liquidus AE and BE. The end of freezing or the beginning of melting of different composition of the system is given by the line PEQ. This line along with AP and BQ forms the **solidus.** Between the solidus and the liquidus, there are two phases, one solid and the liquid in eqm. Hence the system would be monovariant, *i.e.*, for a given temperature composiion is fixed. In the region APE we have solid *A* and solution and in the region BQE there are solid *B* and solution, in equilibrium.

Above the lines AE and BE, the region represents the unsaturated solution. Since there is only one solution phase, the system becomes bivariant. In order to define a system in this area, both the temperature and composition have to be specified. The practical meaning of these curves and areas can be easily understood by considering the behaviour of a given mixture on cooling.

Suppose a mixture with composition (*d*) is taken and heated sufficiently as to give a homogeneous solution represented by point *a*. This liquid may now be slowly cooled. When the temperature will come down to the point *b* on the liquidus, crystals of *A* will begin to separate and will be in equilibrium with a solution saturated with *A* and the temperature is *X*. On further cooling, more and more crystals of *A* would separate. The proportion of *B* in the solution will increase. In other words, with progressive cooling the composition of the saturated solution will change along the curve bE. Thus when the system cools down to the point *c*, the temperature is *y* and the composition of the liquid phase corresponds to z. When the temperature T_E (that of the eutectic) is reached, the other solid *B* also crystallises. The liquid will have the composition as at E, *i.e.*, L. At this constant temperature (T_E) the whole liquid will tend to solidify. The liquid phase will be non-existent below this temperature, and a mixture of *A*-crystals and eutectic solid mixture of *A* and *B* will be formed.

Similar behaviour is also observed if a liquid phase of composition *k* be slowly cooled. At the point *l*, the solid phase *B* will separate in eqm. with its saturated solution, whose composition moves along *lE*. The entire mass will solidify at temperature T_E, giving *B*-crystals and eutectic mixtures of *A* and *B* solids.

The proportions of a solid in eqm. with the liquid phase can also be determined from the diagram. Suppose the system of composition '*a*' is at a temperature *y*. The system will then have pure *A* crystals in eqm. with solution having composition z. The amount of solid separated is proportional to *cz* and the amount of saturated solution present in eqm. is *cy* (of composition z). The ratio of their amounts is *cz*: *cy*. From this ratio and the total weight, it is possible to estimate the expected yield of a solid at a given temperature. We may now take some specific examples of simple eutectic system.

The System Sb-Pb. The two component system of antimony and lead is an example of simple eutectic type, the phase diagram is given in Fig· XVI.7. The melting pt. of pure antimony is 631°C and of pure lead 327°C. With increasing amounts of lead added to antimony, the freezing pt. of the latter is lowered along AE. Likewise BE is the freezing pt. curve of lead with added quantities of antimony. AE and BE form the liquidus of the system. E is the eutectic point (temp. 246°C and composition 87% Pb). ADEFB is the solidus.

Above AEB, the system is one liquid phase only, hence bivariant. Between temperature limits A and D, and composition range D and E, *i.e.*, in the area AED, solid antimony is in equilibrium with solution phase. In the area BEF, solid lead is in equilibrium with solution phase. Below eutectic temp. $T_E = 246°C$, the system will be composed of solid phases of crystals of lead and antimony. If the system has just the eutectic composition (87% lead), it will sharply melt at *E* (T_E=246°C) to form the liquid phase of the same composition. At *E*, solid lead, solid antimony and the solution phase coexist.

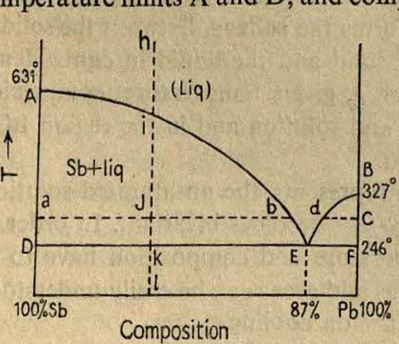


Fig. XVI.7. The phase diagram of Sb-Pb system

If we take the system as at point *h* (*i.e.*, temp. about 700°C and composition about 35% lead), the system will form a liquid phase only. If it is cooled, when the temperature comes down to the point *i* (about 550°C), crystals of antimony will begin to separate. On further cooling, say up to the point *j* (temp. about 300°C), appreciable quantities of Sb-crystals would separate which will remain in equilibrium with solution having a composition as at *b* (*i.e.*, about 80% lead). The proportion of solid: solution = *bj* : *aj* = 16 : 7 (approx). Further lowering of temperature below the point *k*, *i.e.*, below 246°C, the remaining solution will solidify as the eutectic mixture of Sb and Pb-crystals. This gives us a picture of the behaviour of the system with change in temperature.

A lead-silver system also behaves similarly. The phase diagram of this system is given with necessary details in Fig. XVI.7a.

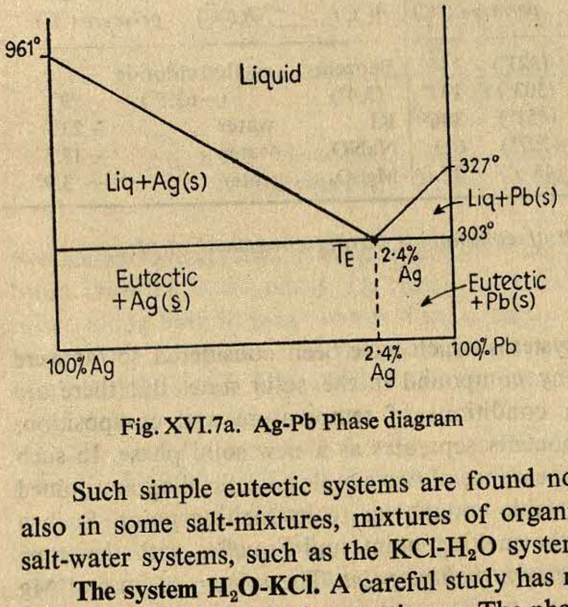


Fig. XVI.7a. Ag-Pb Phase diagram

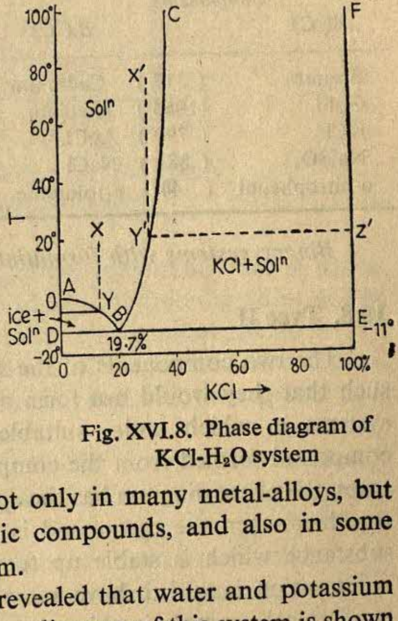


Fig. XVI.8. Phase diagram of $KCl-H_2O$ system

Such simple eutectic systems are found not only in many metal-alloys, but also in some salt-mixtures, mixtures of organic compounds, and also in some salt-water systems, such as the $KCl-H_2O$ system.

The system H_2O-KCl. A careful study has revealed that water and potassium chloride system is a simple eutectic one. The phase diagram of this system is shown in Fig. XVI.8. The two components are not completely miscible in the solution phase in all proportions. That is why the curve liquidus BC cannot reach the other ordinate. There are two solid phases possible KCl and ice (which can separate only below 0°C). The liquidus in the diagram are denoted by AB, BC and the solidus by AD, DE and EF. On cooling a dilute solution of composition *x*, a temperature at the point *y* will be reached when ice crystals would separate out. The residual solution becomes richer in KCl and the freezing pt. changes along yB. At any point *y* in AB pure ice crystals will be in eqm. with a solution of KCl. At a temperature corresponding to *D*(−11°C), KCl-crystals also will begin to separate along with ice. On the other hand on cooling a concentrated solution of composition *x′*, KCl solid begins to separate at *y′*. As more and more KCl separates out, the composition of the saturated solution changes with temperature along *y′*B. Hence the liquidus *CB* is called the solubility curve of KCl in water.

At *B*, where the freezing point curve AB and the solubility curve CB meet, crystals of ice, KCl and also the solution exist together. Hence, the system is non-variant, for $F = C - P + 1 = 2 - 3 + 1 = 0$. This point B is therefore the eutectic point. ($T = -11°C$, 19.7% KCl). In the case of systems where water is one of the components, the eutectic point is generally called the *cryohydric point.* The temperature at B is the cryohydric temperature and the solution of composition B is the cryohydric solution. The solid separating, on freezing, from a cryohydric solution is a mixture of the two solids and not a hydrate compound.

Below are enumerated some of the well studied simple eutectic systems.

TABLE: SIMPLE EUTECTIC SYSTEMS

Components				*Eutectic temperature* (°C)	*Components*		*Eutictic temperature* (°C)
A(°C)		*B*.(°C)			*A*(°C)	*B*.(°C)	
Bismuth	(317°)	Cadmium	(321°)	146°	Benzene	methyl chloride	
Gold	(1064°)	Thallium	(303°)	131°	(5.4°)	(−63.5°)	−79°
KCl	(790°)	AgCl	(451°)	306°	KI	water	−23°
Na_2SO_4	(881°)	NaCl	(797°)	623°	$NaNO_3$	water	−17.5°
o-nitrophenol	(44°)	p-toluidine	(43.6°)	15.6°	$MgSO_4$	water	− 3.9°

Binary systems with formation of compounds having congruent m.pt.

16.8. Type II

The two components of the systems which have been considered so far were such that they would not form any compound in the solid state. But there are systems in which under suitable conditions of temperature and composition, compound formed from the components separates as a new solid phase. In such cases, the phase diagram has the appearance of two simple eutectic diagrams joined together, when the compound is stable enough up to its melting point. Such a substance which is stable up to the melting point and liquefies with the same composition is said to have a *congruent melting point.* The system of Sn and Mg is a typical example in this category.

The system Sn-Mg. The equilibrium diagram of tin (m.p. 232°C) and magnesium (m.p. 651°C) is shown in Fig. XVI. 9. In this diagram P and W represent the freezing points of tin and magnesium. When magnesium is added to tin, the freezing point is lowered along PQ. The points on PQ represent the eqm. between crystals of tin and the liquid alloy. At Q (210°C), in addition to tin crystals, a new solid phase that of a compound of tin and magnesium begins to separate. This point Q is thus an invariant eutectic point having three phases (one liquid and two solids in equilibrium). Further addition of magnesium raises the freezing point along QR and the maximum is reached at R. All along QR from a molten alloy only solid compound will crystallise in eqm. with the liquid. At R, the composition of the liquid and of the solid phase (compound) is the same. This temperature (783°C) is thus the congruent melting point of the compound. Thus PQ is the freezing pt. curve of tin and RQ is the freezing point curve of the compound, The molar composition corresponding to the point R reveals that the compound is Mg_2Sn. Apparently the two branches correspond to a simple eutectic diagram.

On further increasing the percentage of magnesium, the freezing point is lowered again along RS until we reach the second eutectic point *S* (565°C) where

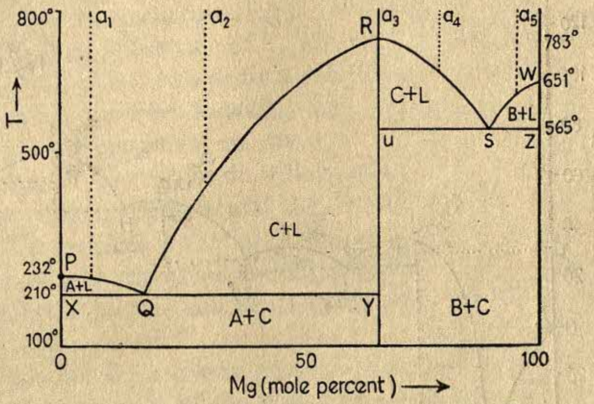


Fig. XVI.9. Phase diagram of the system Sn-Mg,; A—Sn crystals; B—Mg crystals; C—compound Mg_2Sn; L—liquid

two solids—the crystals of magnesium and those of the compound—are in equilibrium with the liquid phase. On further addition of Mg the freezing point will be raised along SW; in other words if tin is added to pure magnesium, its m. pt. will be lowered along WS and on cooling only crystals of magnesium would separate till the point S is reached. The two branches RS and WS thus appear as a simple eutectic system.

The liquidus consists of the curves PQ, QRS, SW whereas, the solidus is comprised of PX, XQY, YR, UZ and ZW. It is predicted from the diagram, the solidus and the liquidus meet at two eutectic points (Q and S). At these eutectic points the solid compound is in equilibrium with either solid tin or solid magnesium. But at no point will solid tin and solid magnesium together will remain in equilibrium with liquid phase.

The overall appearance of the diagram shows a hump in the liquidus at its middle with an eutectic on either side. The existence of such a hump is indicative of the formation of a compound between the components in the solid phase. When the hump has a well-defined maximum, the compound formed is stable and has its melting point at the maximum.

The m.pts. and the eutectic pts. P, R, W and Q, S are invariant, whereas the system is monovariant in the areas PQX, RQY, RUS, WSZ, having a solid and a liquid phase co-existing. Below the solidus, we shall always have a conglomerate of crystals of the compound with magnesium or tin crystals.

When more than one compound is formed, the number of humps in the liquidus will also be greater. There will occur as many humps as there are compounds formed. This is most convincingly illustrated by the two component system ferric chloride and water, in which several solid hydrates are known.

The system Fe_2Cl_6-H_2O. Four different crystalline hydrates of ferric chloride are known. All of these are quite stable, have congruent melting points and have their specific solubilities.

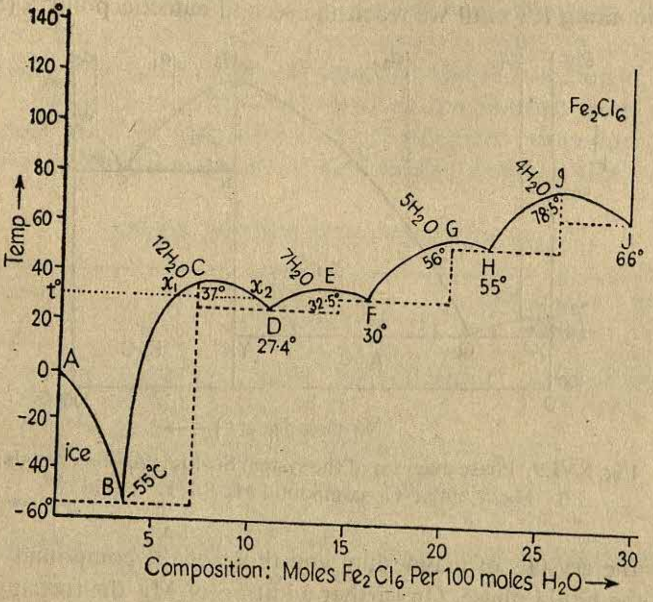


Fig. XVI.10 Phase diagrams of ferric chloride hydrates

Eutectic pts. (°C)

B = ice/$Fe_2Cl_6,12H_2O$ (−55°)
D = $Fe_2Cl_6,12H_2O$/$Fe_2Cl_6,7H_2O$ (27.4°)
F = $Fe_2Cl_6,7H_2O$/$Fe_2Cl_6,5H_2O$ (30°)
H = Fe_2Cl_6, $5H_2O$/Fe_2Cl_6, $4H_2O$ (55°)
J = Fe_2Cl_6, $4H_2O$/Fe_2Cl_6 (66°)

Congruent m. pts.

C = $Fe_2Cl_6,12H_2O$ (37°)
E = $Fe_2Cl_6,7H_2O$ (32.5°)
G = Fe_2Cl_6, $5H_2O$ (56°)
I = Fe_2Cl_6, $4H_2O$ (78.5°)

When small quantities of ferric chloride are added, the freezing pt. of water is lowered. The diagram of the system is shown in Fig. XVI.10. AB represents the freezing pt. curve along which crystals of ice separate. On increasing percentage of Fe_2Cl_6, ultimately the point B is reached at −55°C, when Fe_2Cl_6, $12H_2O$ crystals begin to separate. The point B is thus a eutectic point of solution, ice and Fe_2Cl_6, $12H_2O$. Since one phase is solid ice, it is a cryohydric point.

If solutions of ferric chloride be taken with compositions somewhat higher than that at B, the process of crystallisation would occur even at higher temperatures, so the curve BCD really represents the solubility curve of Fe_2Cl_6, $12H_2O$, with a maximum at C (37°). At this point the liquid and the solid have identical composition and is thus the congruent melting point of dodecahydrate, Fe_2Cl_6, $12H_2O$. From C to D, the solubility diminishes as the proportion of ferric chloride rises. There is thus a distinct hump with maximum at C, indicating the stable compound Fe_2Cl_6, $12H_2O$ formation. When the amount of ferric chloride is raised enough to reach the composition as at D, another solid the heptahydrate,

$Fe_2Cl_6,7H_2O$, begins to crystallise. Pressure kept constant, this point D is eutectic one having the liquid in equilibrium with two solid hydrates, $Fe_2Cl_6,12H_2O$ and $Fe_2Cl_6,7H_2O$.

Both the increase as also the decrease in the proportion of ferric chloride in the solution at C will cause a lowering of solubility, the solid phase crystallising out is Fe_2Cl_6, $12H_2O$ on either side of C. The result is that at a temperature such as t°, the dodecahydrate has two distinct solubilities in water, x_1 and x_2. Such a phenomenon is called *retroflex solubibity* and is observed in systems producing solid compounds with congruent m. pts.

From solutions of ferric-chloride with concentrations higher than that at D, the heptahydrate crystals separate and the solubility curve DEF is like that of dodecahydrate. The point E is the maximum of this portion of the diagram and is the congruent melting point of the heptahydrate (32.5°). The point F (30°) is the eutectic point of hepta- and penta-hydrate crystals along with solution in equilibrium. On the right of F, the solutions will give, on cooling, crystals of pentahydrate. The solubility curve of the pentahydrate is FGH with the maximum at G (56°), the melting point of the pentahydrate crystals. There is yet another hydrate, the tetrahydrate Fe_2Cl_6, $4H_2O$, which separates out from the liquid phase at H (55°). The point H is the eutectic point of penta, tetrahydrate and solution. The solubility curve of tetrahydrate compound is similar to the previous one and is represented by HIJ. This compound melts at 78.5°, which is the maximum of this hump. At J we have the eutectic point of tetrahydrate, anhydrous Fe_2Cl_6 and solution. Beyond J, we have the steep solubility curve of anhydrous Fe_2Cl_6.

In the diagram, the liquidus is given by ABCDEFGHIJ whereas the solidus is given by the dotted lines. The congruent m. pts. C, E, G, I are invariant, so also the eutectic points B, D, F, H, and J.

Binary systems with formation of compounds having incongruent m.pt.

16.9. Type III

In this group are included the systems in which the two components are completely miscible in liquid phase and also produce a compound in the solid state, but the solid compound is not stable up to its melting point. The compound breaks down into a solution and another solid (may be one of the component solid) before reaching its own normal melting point. In other words when the compound (S) is observed to melt, it produces a liquid phase of different composition and a new solid phase (S'). It is said to have an incongruent m. pt. and the change is called a *peritectic change*.

$$S \rightleftharpoons S' + \text{liquid}$$

It is indeed melting with a chemical transformation. The sodium chloride and water system and sodium sulphate-water system are examples of such peritectic change.

The system NaCl-H_2O. The equilibribum diagram of this system is shown in Fig. XVI.11. With addition of NaCl the melting point of ice is lowered and the curve AB represents the freezing point lowering with increase in added NaCl. At B when the temperature is as low as −21°C, a new solid phase namely NaCl,$2H_2O$ also separates out from the solution along with ice. The point B is thus a eutectic point of solution/ice/NaCl,$2H_2O$, often called the cryohydric point. Below this temperature, the system is only solid mixture of ice and NaCl,$2H_2O$. On further increase in the proportion of sodium chloride, the freezing point rises along BC until it reaches C(0.15°C). All along BC, the system is univariant having two phases NaCl,$2H_2O$ and solution in equilibrium. BC is the solubility curve of the dihydrate. It is clear if a solution of composition ‘a’ is cooled, we shall get ice crystals, whereas a solution of composition ‘a′’ on cooling will produce NaCl,$2H_2O$ crystals. At C, a peritectic change takes place. NaCl,$2H_2O$ solid is no longer stable above 0.15°C and it changes into anhydrous NaCl and the solution. The curve CD is the solubility curve of NaCl. The point C is the incongruent melting point of NaCl,$2H_2O$. The regions of stability of the different solid phases are indicated in the diagram.

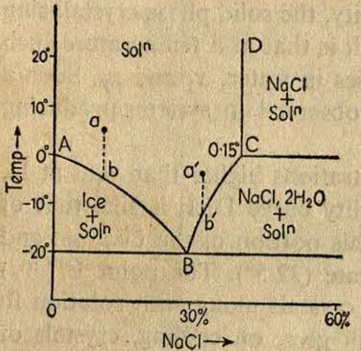


Fig. XVI.11. The system NaCl and H_2O

Freezing mixtures. There are other facts which become obvious from the diagram. Firstly, we cannot have a solution of NaCl at a temperature lower than the cryohydric temperature. Any solution taken to a lower temperature, being unstable, would change into a solid mixture of ice and NaCl, $2H_2O$. At a temperature above the cryohydric temperature, ice can exist in eqm. with solution of one composition and salt with solution of another composition.

Secondly, if we mix ice, salt and water at about say, 0°C water will dissolve the salt and if the saturated solution is quite concentrated, ice will begin to melt. In the melting of ice heat will be absorbed and temperature will go down. The salt solution, now being diluted, will dissolve more salt which will induce more ice to melt. In this way, due to abstraction of heat, temperature will fall till the cryohydric temperature −21°C is reached. The mixture will remain at this temperature until all the ice melts or all the salt dissolves. Ice and salt mixtures thus lead spontaneously to low temperatures, which is of wide application in domestic and commercial requirement as easily available freezing mixtures. Not only mixtures of common salt and ice serve as freezing mixtures but other salts with ice may also be used to attain low temperatures, *e.g.*, NH_4Cl/Ice (−15°), NH_4NO_3/ice (−17°), $NaNO_3$/ice (−18°), $CaCl_2$/ice (−55°), alcohol/solid CO_2 (−72°) etc.

The system Na_2SO_4-H_2O. The behaviour met with this system is graphically illustrated in Fig. XVI. 12. The possible solid phases are ice, Na_2SO_4,$10H_2O$; Na_2SO_4,$7H_2O$; Na_2SO_4, of which the heptahydrate is unstable in presence of the solution. On adding sodium sulphate to water, the freezing point is lowered. The curve AB is the freezing point curve, along which ice separates out from dilute solutions. When the concentration is increased to reach the point B, a new solid phase

Na_2SO_4, $10H_2O$ is formed. The point B is then a non-variant eutectic or cryohydric point having three phases, solution, ice and decahydrate. The curve BD gives the temperature at which Na_2SO_4, $10H_2O$ separates out from comparatively more

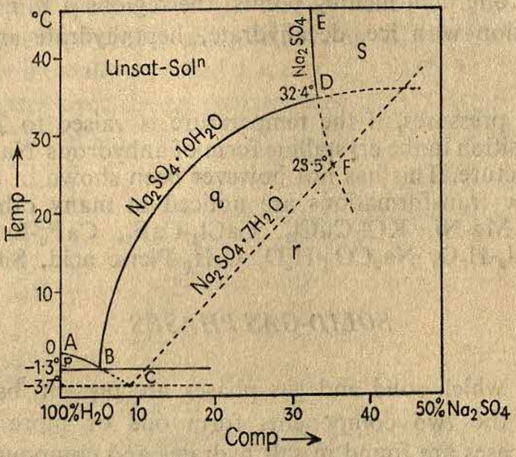


Fig. XVI.12. Phase diagram of sodium sulphate and water system

concentrated solutions. BD is the solubility curve for the decahydrate. At the point D, the decahydrate $Na_2SO_4,10H_2O$ suffers a peritectic change, so the decahydrate does not reach its normal melting point. In the peritectic transformation,

$$Na_2SO_4,\ 10H_2O \rightleftharpoons Na_2SO_4 + \text{Solution},$$

the anhydrous solid Na_2SO_4 is obtained along with a solution of the salt. That is, D is the incongruent m. pt. of the compound Na_2SO_4, $10H_2O$, and at this point there are three phases at equilibrium the solution, decahydrate and anhydrous solid Na_2SO_4. Hence the point, D represents a non-variant condition for the system; the temperature is 32.38°C, composition 33.2% Na_2SO_4. Above this temperature, the solid separating from saturated solutions is always anhydrous Na_2SO_4. The curve DE is the solubility curve of anhydrous Na_2SO_4.

When a saturated solution of sodium sulphate is cooled, along ED anhydrous salt separates. On reaching the point D, decahydrate crystals would begin to separate. This is rather a slow process and if a little alcohol is added, the deposit of decahydrate may be prevented and the saturated solution remains metastable and continues deposit of Na_2SO_4 till the point F is reached when heptahydrate crystals separate out at 23.5°C. This is formed only in absence of decahydrate and the heptahydrate has a spontaneous tendency to be transformed into decahydrate. The metastable conditions are indicated by broken lines. The curve CF denotes the solubility of heptahydrate. At F, the solid hepathydrate changes into anhydrous Na_2SO_4 and solution. So this is again an incongruent melting point, that of heptahydrate. Although the curves BD and CF can be followed, by supersaturation, beyond D and F to some extent but the point of equilibrium of the hepta and decahydrate with solution cannot be experimentally realised. As evident from the diagram the solubility of the metastable heptahydrate is more than that of the stable decahydrate, which is a thermodynamical necessity.

In the diagram, B and C are the non-variant cryohydric points, D and F are the non-variant incongruent melting points; the regions *p*, *q*, *r* and *s* are areas of equilibria of solution with ice, decahydrate, heptahydrate and anhydrous salt respectively.

Under higher pressures, if the temperature is raised to 234°C there would occur another transition in the crystalline form of anhydrous Na_2SO_4 from rhombic to monoclinic structure. This has not however been shown in the diagram.

Such peritectic transformations are noticed in many other binary systems such as, Au-Sb, Mg-Ni, KCl-$CuCl_2$, $CaCl_2$-CaF_2, CaF_2-BeF_2, K_2SO_4-$CdSO_4$, $MgSO_4$-H_2O, $CaCl_2$-H_2O, Na_2CO_3-H_2O, C_6H_6-Picric acid, SiO_2-Al_2O_3

SOLID-GAS PHASES

Binary systems, in which solid and gas phases are present, become of notable importance when the two components form one or more compounds in the solid phase. Such cases are found in salt hydrates and compounds like argentammino chlorides (AgCl, $x$$NH_3$) etc. In studying the equilibria in such systems it is convenient to follow up the pressure variations with composition. We may exemplify this with the salt-hydrate system $CuSO_4$ and H_2O.

With these two components—$CuSO_4$ and H_2O—thre are, under different conditions, four solid phases and the vapour phase is one of water. The solid phases are: (*i*) $CuSO_4, 5H_2O$, (*ii*) $CuSO_4, 3H_2O$, (*iii*) $CuSO_4, H_2O$ and (*iv*) anhydrous $CuSO_4$. When water vapour is gradually led into the system containing anhydrous $CuSO_4$ or when the pentahydrate $CuSO_4, 5H_2O$ is gradually dehydrated, the following equilibria are envisaged:

	eqm constants
I $CuSO_4, 5H_2O \rightleftharpoons CuSO_4, 3H_2O + 2H_2O$	$K_1 = P_I = 45.4$ mm
II $CuSO_4, 3H_2O \rightleftharpoons CuSO_4,H_2O + 2H_2O$	$K_2 = P_{II} = 30.9$ mm
III $CuSO_4, H_2O \rightleftharpoons CuSO_4 + H_2O$	$K_3 = P_{III} = 4.5$ mm

If P_I P_{II} and P_{III} denote the corresponding equilibrium pressures of water vapour, applying law of mass action, we know that

$$\frac{P_I^2 \times P_{tri}}{P_{penta}} = K_1' \quad \text{or} \quad P_I = K_1$$

Similarly, the vapour pressures for other equilibria are also constant at a given temperature. This indeed is realised in practice. When pentahydrate crystals are enclosed in a vessel, kept at a constant temperature (say 50°C) and the vapour is continuously removed by means of a pump, the vapour pressure is found to remain constant at 45.4 mm. We have really three phases in the system now, solid pentahydrate, solid trihydrate and the water vapour. So,

$$F = C - P + 2 = 2 - 3 + 2 = 1$$

i.e., the system is univariant. Since the temperature is defined to be constant, the pressure cannot vary so long as the three phases co-exist. This pressure is often mentioned as the vapour pressure of the hydrate $CuSO_4,5H_2O$ which is somewhat misleading. It is really the pressure of water vapour when it is in equilibrium with two phases $CuSO_4,5H_2O$ and $CuSO_4,3H_2O$. The constancy of the pressure is shown in the experimentally recorded diagram (Fig. XVI. 13) in which along *ab* the equilibrium presssure over the tri-pentahydrate system remains constant.

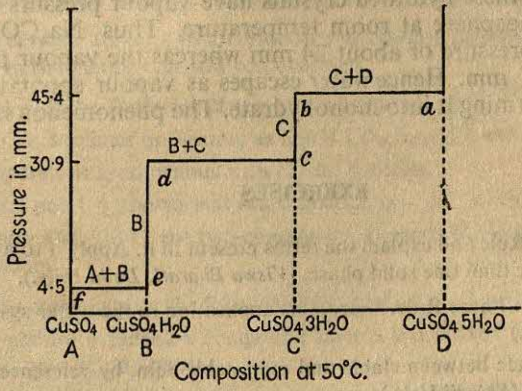


Fig. XVI.13. The dehydration of $CuSO_4$, $5H_2O$ at 50°C

At *b* the pentahydrate is entirely dehydrated to trihydrate and as the system now contains only one solid phase with vapour. The system is now bivariant. At this stage the pressure drops down to *c* (30.9 mm). Along *cd*, the pressure again remains constant as trihydrate loses water and is slowly dehydrated to monohydrate ($F = 1$). When the point *d* is reached, the composition shows it is only monohydrate, the system becomes bivariant and the pressure falls to *e* (4.5 mm).

With continued removal of H_2O-vapour, the monohydrate crystals are slowly converted into anhydrous sulphate along *ef*. The pressure during the process remains constant, for, again two solids and one vapour phase remain together to make the system univariant. When the whole of water is removed, the pressure drops down to zero.

The diagram has a stepwise configuration. Such step-wise vapour-pressure-composition diagrams are indicative of the formation of compounds between the components which may not be isolated or prepared experimentally. The number of steps would also indicate the number of compounds formed between the components.

Deliquescence and Efflorescence. When a crystalline *substance* on standing in air forms a solution by absorbing water vapour from the atmosphere it is said to deliquesce. $CaCl_2,6H_2O$ or $NaOH,H_2O$ etc. are highly deliquescent.

In our laboratories the temperature is about 20°C so that the vapour pressure of water is about 17 mm. If some $CaCl_2,6H_2O$ be kept exposed in air, it absorbs water and as it is highly soluble, a saturated solution is formed. The vapour pressure of sat. solution of calcium chloride is quite low, about 7-8 mm at 20°C. This is much lower than the vapour-pressure of water in the atmosphere. The result is, more and more water is absorbed and the solution becomes more and more dilute. This continues till the vap-pressure of the solution is equal to that of the water in the atmosphere. Hence a substance to behave as deliquescent must be a very soluble one having a low vapour pressure of its saturated solution.

On the other hand there are hydrated crystals such as $Na_2CO_3,10H_2O$, sodium carbonate decahydrate, which give up their water of hydration to the atmosphere and in the process disintegrate into dehydrated products spontaneously. This is due to the fact that these hydrated crystals have vapour pressurs greater than that of water in the atmosphere at room temperature. Thus $Na_2CO_3,10H_2O$ crystals have eqm. vapour pressure of about 24 mm whereas the vapour pressure of water at 20°C is about 17 mm. Hence water escapes as vapour spontaneously from the decahydrate transforming it into monohydrate. The phenomenon is efflorescence.

EXERCISES

1. State the Phase Rule and explain the terms present in it. Apply it to a system of one component comprising more than one solid phase. (*Viswa Bharati, Delhi Univ.*).

2. State and explain Phase Rule. Discuss its application to the water system (*Bombay Univ., Agra Univ., Dacca Univ.*)

Explain the difference between stable and metastable eqm. by reference to vapour-pressure curves of water and ice. (*Shivaji Univ.*).

3. Draw a phase diagram for the sulphur system and give its main features in a chart. Explain the terms stable and metastable equilibrium. What is the effect of pressure on (*i*) the transition temperature of rhombic sulphur and (*ii*) the melting point of monoclinic sulphur? (*Guru Nanak Univ.*).

4. Discuss the phase diagram of lead-silver system. Explain briefly its important features. (*Punjab Univ.*).

5. Define and illustrate: (*i*) cryohydrate (*ii*) eutectic point (*iii*) liquidus (*iv*) peritectic change (*v*) retroflex solubility (*vi*) Triple point.

6. What changes you expect to observe when the following are cooled progressively:—
(*i*) dilute solution of NaCl and a conc. solution of NaCl
(*ii*) a conc. solution of NaCl and a conc. solution KCl.

7. Discuss the behaviour of a liquid melt of two metallic components on cooling (*a*) when no compound is formed, (*b*) when compounds are formed.

8. What types of phase diagrams would you construct for a system of water and a salt which gives two or more hydrates? What informations can be obtained from these diagrams?

9. The freezing points of mother mixtures of *A* and *B* of different compositions are given below:

Mole% A	100	90	80	70	60	50	40	30	20	10	0
f. pt. °C	65	60	50	35	50	55	50	35	20	30	35

Draw and interpret the phase diagrams for the system.State the changes that will occur if a mixture of 40 mole% A is gradually cooled from 60°C to 10°C. (C.U. 1974)

10. Construct phase diagram for the condensed system of A and B which form a simple eutectic. The f.pt. of A is 80°C and that of B 121°C. The eutectic temperature is 50°C. Label the phases present. What is the number of degrees of freedom at the eutectic point?
(*Madras Univ.*)

11. Explain why
    (*a*) a mixture of tin and lead is used for soldering
    (*b*) ice and salt mixture is used as refrigerant
    (*c*) Dry ice is preferred to ice-salt mixture as refrigerant
    (*d*) fusion mixture is used instead of Na_2CO_3 in dry tests?

12. What are meant by the term 'efflorescence' and 'deliquescence'? Give reasons to explain why
    (*i*) $Na_2SO_4,10H_2O$ is efflorescent but $CaCl_2$, $6H_2O$ is deliquescent
    (*ii*) On heating iodine sublimes but sulphur melts at ordinary pressure.

13. Blue vitriol crystals are kept in a desiccator, to which a manometer is attached What progressive changes in the manometer will you observe?

14. Justify or correct the following statements with reasonings:
    (*i*) Solid CO_2 sublimes on heating as liquid CO_2 does not exist
    (*ii*) Cryohydrate is synonymous with crystal hydrates
    (*iii*) Eutectic point is non-variant but transition point is univariant
    (*iv*) At 1 atm and 120°C, the two-component system—N_2 and H_2O—has two degrees of freedom.

15. Make critical comments on the following statements:

(*a*) A eutectic mixture is indeed a compound since it has a fixed m.pt and has the same composition in solid and liquid states

(*b*) Common salt is sprayed over snow-covered streets in cold countries in order to harden the surface

(*c*) Calcium chloride crystallises as hydrated salt but sodium chloride has no hydrated form.

CHAPTER 17

CHEMICAL KINETICS

17.1. Chemical Kinetics

Chemical kinetics deals with the *speed* or *rate* at which a reaction occurs and the mechanism by which they proceed. In studying equilibria, the initial and final states were only considered, the energy-relations between the reactants and resultants being governed by thermodynamics where the time or intermediate steps were of no concern. In kinetics, the speed of the process is followed and hence time variable is introduced. Such studies, it will be seen, reveal the influence of different factors on the progress of the reaction as also the way or mechanism through which the chemical changes occur.

Besides the chemical nature of the reactants, the rates of reaction also depend on the concentration of reactants and the temperature. These will be considered here. The influence of foreign substances (catalysts) or that of radiations (photo chemical reactions) will be dealt with later.

Rate of a Reaction. The rate of a reaction, *i.e.*, the velocity of a reaction is the amount of chemical change occurring per unit time. The rate is generally expressed as the decrease in concentration of a reactant or as the increase in concentration of a product per unit time. So, if 'c' is the concentration of a chosen reactant at any time t, the rate is $-\frac{dc}{dt}$. Or, if the concentration of a product be x at any time t, the rate would be $\frac{dx}{dt}$. The reactant or the product chosen should be specified. The time is usually expressed in seconds. The rate will have units of concentration divided by time. The concentrations are taken in gm-moles/litre, hence rate is moles per litre per second.

With the progress of time, the concentration of the reactant (C) continuously decreases and hence the rate of reaction ($-dc/dt$) also decreases with time.

The velocity of reaction is very sensitive to temperature. The rate is invariably studied at a constant temperature by maintaining the system in a thermostat.

Measurement of Reaction Rates: Some reactions, such as the ionic reactions or the explosive reactions, occur almost instantaneously. On the other hand, there are reactions which occur so slowly that months and years are needed for any measurable amount of transformation. To measure the rates of such reactions is quite difficult although some special techniques have recently been developed and applied in measuring the rates of some fast reactions. In between the very fast and very slow reactions, there are many reactions, such as the decomposition of H_2O_2, HI, N_2O_5, etc. or hydrolysis of ester, and many other organic and inorganic changes, for which the speed can be easily measured. To measure the rate, the decrease in concentration of one or more of the reactants or the increase in concentration of a product is followed at different time intervals. Both chemical and physical methods of analysis are employed for such measurements according to suitability.

In chemical methods, definite volumes of samples are separated or pipetted out from the reaction mixture from time to time. The samples are immediately chilled and diluted with inert media so as to 'freeze' the reaction. The freezing of the reaction means abruptly slowing down the reaction or practically stopping the reaction in the separated sample. These samples are then quickly estimated, very often by titration with suitable reagents.

Use of physical methods is often taken recourse to as these are more convenient and accurate. The physical measurement is made with the reaction mixture as such and the change in concentration of the reactant or the product with time is deduced directly therefrom. Any physical property of a constituent of the system which changes with the progress of reaction may be taken advantage of. Very frequently, optical rotation, optical density with a specific wavelength, conductivity, refractive index, dielectric constant, colorimetry, light-scattering, etc. are measured to pursue the variation in concentration with time. In gaseous reactions, the pressure-changes at constant volume may be followed at different time intervals.

17.2. Order of a Reaction

The order of a reaction is the number of concentration terms on which its reaction rate is experimentally found to depend. Thus if the rate of a reaction is observed to depend on the first power of the concentration of the reactant, *i.e.*

$$\text{Rate} = kC$$

then the reaction is said to be of the *first order*. k is called the velocity constant or specific reaction rate. It expresses the velocity if the reactant (s) be at unit concentration.

When the rate is proportional to the product of two reactant concentrations or the square of the concentration of a reactant, the reaction is of the *second order*. For example, the decomposition of hydroiodic acid, $2HI \rightarrow H_2 + I_2$, is given by,

$$\text{Rate} = kC^2_{HI}$$

and the hydrogen-iodine reaction, $H_2 + I_2 \rightarrow 2HI$, is found to follow,

$$\text{Rate} = kC_{H_2}C_{I_2}$$

Both are second order reactions. Hence, if the reaction rate is *experimentally found* to be represented by

$$-\frac{dc}{dt} = kC^n \qquad \ldots \text{(XVII.1)}$$

the order of the reaction is n. Generally speaking, if several reactants A, B, C, etc. are involved and it is *observed experimentally* that the rate of the process is given by

$$\frac{-dc}{dt} = kC_A^{\alpha}C_B^{\beta}C_C^{\gamma}\ldots, \qquad \ldots \text{(XVII.2)}$$

then the order of the reaction would be $n = \alpha + \beta + \gamma + \ldots$. The reaction is said to be of the α-th order with respect to A, the β-th order with respect to B, etc.

The order to a reaction may thus be defined as the sum of the exponents of the concentration terms in the rate equation.

Though theoretically reactions of high order are possible, but it is doubtful if reactions higher than the third order exist. But there are reactions in which the order is *fractional*, *i.e.*, $n = \frac{1}{2}, \frac{3}{2}$, etc. For instance, the ortho-para hydrogen conversion has its rate expressed by $\frac{-d[H_2]}{dt} = kC_{H_2}^{3/2}$

In some heterogeneous or surface reactions, the rate has been found to be independent of concentration. These are *zero-order reactions*. It is important to realise that the order of a reaction and the rate equations are derived from experimental results. Any attempt or theory proposed to explain the mechanism of a chemical process must satisfy the rate equations experimentally observed.

It is also seen that there is no necessary connection between the kinetic order and the form of the stoichiometric equation of a reaction.

For the reaction, $2N_2O_5 \rightarrow 4NO_2 + O_2$, the order is one. Again, for the reaction $CH_3CHO \rightarrow CH_4 + CO$, the order is three halves (3/2).

17.3. Molecularity of a Reaction

In early days, no distinction was made between the order and the molecularity of a reaction, they were synonymous. The first order reactions were *unimolecular*, the second order *bimolecular* and so on. But the term molecularity, as distinct from the order of a reaction, is now expressed differently and is linked to the mechanism of a chemical process.

From the standpoint of kinetics, the chemical reactions are considered to belong to two categories: Elementary reactions and Complex reactions. The relatively simple reactions in which the reactants are directly transformed into products without any intermediate steps are the Elementary reactions. To illustrate

(*i*) $H_2 + I_2 \rightarrow 2HI$; (*ii*) $\underset{\text{cyclobutane}}{C_4H_8} \rightarrow 2C_2H_4$;

(*iii*) $CH_3Br + AgOH \rightarrow CH_3OH + AgBr$

(*iv*) $CH_3COOEt + H_2O \rightarrow CH_3COOH + EtOH$ etc. etc.

The minimum total number of molecules required for the occurrence of the process is its 'molecularity'.

On the other hand, the Complex reactions take place through some successive or consecutive steps till the final products are formed. Each of the consecutive steps is an elementary process. For example, the decomposition of N_2O_5 is now known to proceed as follows:

$$\begin{aligned}
&(i)\ N_2O_5 \rightarrow NO_2 + NO_3\\
&(ii)\ NO_2 + NO_3 \rightarrow NO + O_2 + NO_2\\
&(iii)\ \underline{NO + N_2O_5 \rightarrow 3NO_2}\\
&\quad\ \ 2N_2O_5 \rightarrow 4NO_2 + O_2
\end{aligned}$$

The reaction is experimentally found to be of the first order.

Now each step or elementary process has its molecularity, which is the total number of entities (molecules, atoms, radicals) participating in the process. In this case, some steps are bimolecular and one unimolecular. As such it is not desirable to express the molecularity of the overall reaction, as one step may involve one molecule, another two molecules, etc. The molecularity must be integral whereas the order may be fractional also. The order is obtained from the observed rate of reaction whereas the molecularity is based on the proposed mechanism which should satisfy the experimental findings. There is no correlation between the order and the molecularity of the reaction or between the stoichiometric representation and the molecularity, as seen in the example of N_2O_5 decomposition cited above. Very often, the slowest step in a sequence of steps of a reaction determines its order.

BASIC KINETIC LAWS

17.4. First Order Kinetics

A reaction of the first order is represented as

$$X \rightarrow Y$$

The rate of the reaction will be directly proportional to the concentration of the reactant, *i.e.*,

$$\frac{-dC}{dt} = kC\,; \quad \text{or} \quad \frac{-dC}{C} = kdt \qquad \ldots (\text{XVII.3})$$

in which C is the concentration of the reactant at any time t and k is a constant, called the *velocity constant* or *specific reaction rate.*

On integration, $-ln\, C = kt + z$ (constant).

If at the start of the reaction, the initial concentration of the reactant is C_0, then we have at $t = 0$, $C = C_0$.

Substituting, $-ln\, C_0 = z$

$\therefore$ $-ln\, C = kt - ln\, C_0$

Hence $ln\,\frac{C_0}{C} = kt$, or $\frac{C}{C_0} = e^{-kt}$

$$\therefore \quad C = C_0 e^{-kt} \qquad \ldots (\text{XVII.4})$$

The concentration (C) therefore diminishes exponentially with time.

We may also write, $C_0 - C = C_0[1 - e^{-kt}]$ . . . (XVII.4a)

The rate equation may also be conveniently expressed in an alternative form, by expressing the rate in terms of the product. When x moles per unit volume of product Y is formed from the reactant, the concentration of the reactant is $a-x$, when a is the initial concentration of the reactant. So,

$$\frac{dx}{dt} = kC = k(a-x)$$

i.e.

$$\frac{dx}{a-x} = kdt$$

On integration, $-ln\,(a-x) = kt + z'$ (constant)

When $t = 0, x = 0$, hence $-\,ln\,a = z'$

$$\therefore \qquad -ln(a-x) = kt - ln\,a$$

i.e.,
$$k = \frac{1}{t}\,ln\,\frac{a}{a-x} \qquad \ldots \text{(XVII.5)}$$

or
$$x = a\,(1-e^{-kt})$$

It is obvious that equation XVII.4a and XVII.5 are the same.

If x_1 and x_2 are the concentrations of product at time t_1 and t_2, then the corresponding concentrations of unchanged reactants would be $(a-x_1)$ and $(a-x_2)$. So,

$$kt_1 = ln\,\frac{a}{a-x_1} \text{ and } kt_2 = ln\,\frac{a}{a-x_2}$$

$$\therefore \qquad k\,(t_2-t_1) = ln\,\frac{a-x_1}{a-x_2}, \text{ or } k = \frac{1}{t_2-t_1}\,ln\,\frac{a-x_1}{a-x_2} \qquad \ldots \text{(XVII.6)}$$

Some interesting characteristics of the first order reactions are:

(*i*) In a first order reaction, $C = C_0e^{-kt}$; a first order reaction cannot be complete; for, C would become zero only at infinite time t.

(*ii*) The quantity $\frac{a}{a-x}\left(\text{or } \frac{C_0}{C}\right)$ is a ratio of concentrations, so its value will be the same whatever units are employed to express the concentrations, e.g., moles per litre, gms per c.c., partial pressures etc. It follows that the velocity constant $k\left(= \frac{1}{t}\,ln\,\frac{a}{a-x}\right)$ will have the dimension of reciprocal time, sec^{-1}.

(*iii*) The equation (XVII.5) is $ln\,(a-x) = -kt + ln\,a$

$$\text{or} \quad \log\,(a-x) = -(k/2.303)t + \log a$$

If $\log\,(a-x)$ is plotted graphically against time, it would give a straight line. So when a plot constructed from experimental values of $\log\,(a-x)$ and t is found to be linear, the reaction is of the first order. The slope of the line is $-k/2.303$ from which the velocity constant k is known.

(*iv*) The time required for half the reactant to change can be easily evaluated. Let $t_{\frac{1}{2}}$ be the time required when $x = a/2$.

$$\text{Then } t_{\frac{1}{2}} = \frac{1}{k}\,ln\,\frac{a}{a-x} = \frac{1}{k} \times ln\,\frac{a}{a/2} = \frac{2.303 \log 2}{k} = \frac{0.693}{k} \qquad \ldots \text{(XVII.6a)}$$

The period of half-decomposition is thus a constant for a given reaction and is independent of initial concentration. The time required is often called *half value period*, or *half-life*.

Not only half-value period, the time necessary to complete any definite fraction (ϕ) of the reaction is also independent of the initial concentration in first order kinetics.

The first order reactions are recognised from these characteristics.

Examples of first order reactions: Quite a number of homogeneous gaseous reactions have been found to be of the first order. The thermal dissociation of nitrogen pentoxide, acetone, azocompounds, aliphatic ethers follow first order kinetics. The same is also found in the conversion of N-chloroacetanilide into *p*-chloroacetanilide (Blanksma, 1902); the individual radioactive changes are also of the 1st order. Many racemisations are also first order changes.

(*a*) $2N_2O_5 \rightarrow 4NO_2 + O_2$

(*b*) $C_3H_7\text{-}N{=}N\text{-}C_3H_7 \rightarrow C_6H_{14} + N_2$

(*c*) $CH_3CH_2Br \rightarrow C_2H_4 + HBr$

(*d*) Cyclohexyl bromide → Cyclohexene + HBr

(*e*) $2H_2O_2 \rightarrow 2H_2O + O_2$

A few experimental findings are quoted below:

(*i*) Daniels and Eyring studied the decomposition of N_2O_5 in CCl_4 solvent. The progress of reaction was followed by measuring the volume of evolved oxygen with time. Oxygen being insoluble in CCl_4 escaped from the solution; other oxides of nitrogen remained in solution.

Since two molecules of N_2O_5 on decomposition liberates one molecule of oxygen, if V and V_∞ denote the volumes of oxygen given out at any time t and at the completion of reaction, then $(V_\infty - V)$ is proportional to the amount of undecomposed N_2O_5 at time t. It is easily seen,

$$k = \frac{2.303}{t} \log \frac{V_\infty}{V_\infty - V},$$

provided it is of the 1st order. Substitution of experimental data revealed a constancy in the value of k, confirming first order kinetics.

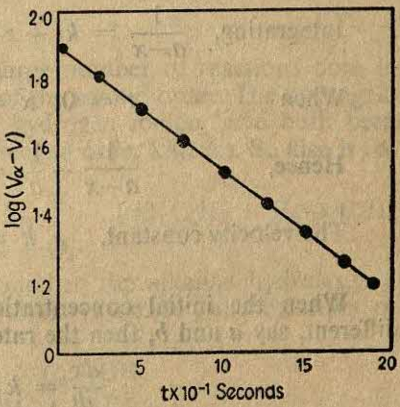


Fig. XVII.1.
[Decomposition of N_2O_5 in CCl_4 soln

TABLE: DECOMPOSITION OF N_2O_5 IN CCl_4 SOLUTION (30°C)

Time (sec)	$(V_\infty - V)$ *c.c.*	*log* $(V_\infty - V)$	*k* (sec^{-1})
0	84.85	1.9827	—
2400	69.20	1.8401	0.000085
4800	57.20	1.7574	0.000082
7200	47.15	1.6735	0.000081
9600	39.00	1.5911	0.000081
12000	32.18	1.5076	0.000081

The plot of log $(V_\infty - V)$ against time t gives a straight line as in Fig. XVII.1 and the value of k derived from the slope of the line agrees well with those recorded above.

(*ii*) The conversion N-chloroacetanilide to *p*-chloroacetanilide has also been completely studied and found to be of the first order. The reaction was followed by estimating the reactant N-chloroacetanilide with KI at different time intervals.

$$C_6H_5(Cl)NCOCH_3 \rightarrow p\text{-}Cl\text{-}C_6H_4NHCOCH_3$$

N-chloro compound liberates iodine from KI which is titrated with standard thiosulphate. The para-chloro compound does not liberate iodine from potassium iodide. The titre value gives the amount of $(a-x)$ at any time t (see problem 3).

17.5. Second Order Kinetics

A reaction will be of the second order when the reaction rate would be found to depend upon the product of two concentrations. This may arise in two ways:

$$(i)\ \underset{(a-x)}{2A} \rightarrow \text{Products} \qquad (ii)\ \underset{(a-x)}{A} + \underset{(b-x)}{B} \rightarrow \text{Products}$$

If the two substances have the same initial concentration (a) and if x denotes the concentration of the reactants which disappears in time t, then the rate will be

$$\frac{dx}{dt} = k(a-x)^2\ ; \quad \text{or} \quad \frac{dx}{(a-x)^2} = kdt \qquad \ldots \text{(XVII.7)}$$

Integrating, $\dfrac{1}{a-x} = kt + z$ (constant)

When $t = 0,\ x = 0;\ \therefore\ \dfrac{1}{a} = z$

Hence, $\dfrac{1}{a-x} - \dfrac{1}{a} = kt$

The velocity constant, $k = \dfrac{x}{at(a-x)}$ $\ldots$ (XVII.8)

When the initial concentrations of the two substances participating are different, say a and b, then the rate is given by

$$\frac{dx}{dt} = k\,(a-x)\,(b-x) \qquad \ldots \text{(XVII.9)}$$

where x is the amount of any reactant transformed in time t.

Rewriting, $\dfrac{dx}{(a-x)(b-x)} = kdt$

or $\dfrac{1}{a-b}\left[\dfrac{1}{b-x} - \dfrac{1}{a-x}\right] dx = kdt$

Integrating, $\dfrac{1}{a-b}\,ln\,\dfrac{a-x}{b-x} = kt + z$, (a constant)

When $t = 0, x = 0$, therefore $\dfrac{1}{a-b}\,ln\,\dfrac{a}{b} = z$

Substituting $\dfrac{1}{a-b}\,ln\,\dfrac{a-x}{b-x} - \dfrac{1}{a-b}\,ln\,\dfrac{a}{b} = kt$

or $k = \dfrac{1}{t(a-b)}\,ln\,\dfrac{b(a-x)}{a(b-x)}$ $\ldots$ (XVII.10)

It may also be written as $t = \dfrac{2.303}{k(a-b)}\log\dfrac{b(a-x)}{a(b-x)}$,

which means that the plot of $\log\dfrac{b(a-x)}{a(b-x)}$ against t for such a reaction would be linear, a fact which has been corroborated by experimental observation in many second order reactions. The straight line would pass through the origin and from its slope $2.303/k(a-b)$, the velocity constant would be obtained.

(*i*) The value of k would depend on the units employed in expressing a and b, for, the magnitudes of $(a-b)$ would depend on the units used.

(*ii*) In a second order reaction where the two initial concentrations are the same, the equation (XVII.8) is applicable. The half value period ($t_{\frac{1}{2}}$) for a 2nd order reaction is given by

$$t_{\frac{1}{2}} = \frac{x}{ak(a-x)} = \frac{a/2}{a.k.a/2} = \frac{1}{ak} \qquad \text{. . . (XVII.11)}$$

i.e., the time required for half the amount of reactant to undergo the change is inversely proportional to the initial concentration (a), whereas in first order reactions $t_{\frac{1}{2}}$ is constant.

Examples of Second Order Reactions. A large number of reactions both in gas and in liquid phases have been found to be of the second order. The hydrogen-iodine reaction as also the decomposition of hydrogen iodide have both been studied thoroughly and observed to follow the second order kinetics. So also is the hydrogenation of ethylene.

(*i*) $H_2 + I_2 \rightarrow 2HI$, (*ii*) $2HI \rightarrow H_2 + I_2$, (*iii*) $C_2H_4 + H_2 \rightarrow C_2H_6$

(*v*) $2O_3 \rightarrow 3O_2$ (*iv*) $2NO_2 \rightarrow 2NO + O_2$

Examples of second order reactions are found in the alkaline hydrolysis of ester, the esterification of acids, alkaline hydrolysis of amides, dizaotisation of many amines etc.

(*i*) $CH_3COOC_2H_5 + OH^- \rightarrow CH_3COO^- + C_2H_5OH$

(*ii*) $CH_3COOH + CH_3OH \rightarrow CH_3COOCH_3 + H_2O$,

(*iii*) $OH^- + CH_3I \rightarrow CH_3OH + I^-$

(*iv*) $2C_6H_5CHO \rightarrow C_6H_5CHOHCOC_6H_5$

In following the kinetics of alkaline hydrolysis of esters, known concentrations of ester (a) and alkali (b) are taken in a mixture. The amount of alkali consumed in the reaction at different times is followed by withdrawing samples and titrating the same with a standard acid. Thus x is known and hence $(a-x)$ and $(b-x)$ are also known. The velocity constant k is then calculated with equation (XVII.10).

17.6. Pseudo-unimolecular Reactions

There are a number of reactions which follow the first order kinetics though more than one kind of reactants are involved in the reaction. Common examples are the inversion of cane sugar or the hydrolysis of an ester in an acid medium.

(*i*) $C_{12}H_{22}O_{11} + H_2O = 2C_6H_{12}O_6$

(*ii*) $CH_3COOEt + H_2O = CH_3COOH + EtOH$

These are truly second-order reactions. Two substances water and canesugar, or water and ester participate, but the rate of reaction is experimentally observed to depend only on the conc. of cane sugar or of ester.

A second-order reaction is governed by the eqn. XVII.10. If the conc. of one of the participants is very large compared to that of the other, say $b \gg a$, then

$b-x \approx b$, and $a-b \approx -b$, which is practically constant. Hence, eqn. XVII.10 reduces to

$$kb = \frac{1}{t}\, ln \frac{a}{a-x}, \quad \text{or} \quad k' = \frac{1}{t}\, ln \frac{a}{a-x}$$

That is, under these circumstances, the reaction will follow first order kinetics.

In the reactions cited above, water is present in such large excess, that even if the reaction is complete, the conc. of water would virtually remain unaltered.

So that, $$-dc/dt = kC_{\mathrm{sugar}}C_{\mathrm{H_2O}} = k'C_{\mathrm{sugar}}$$

As such these reactions follow first order kinetics. Such reactions since old days have been mentioned in literature as *pseudo unimolecular reactions.*

The progress of the inversion of cane sugar with time is followed polarimetrically. Canesugar solution rotates the plane of polarisation to the right, whereas the mixture of glucose and laevulose produced has a rotation to the left. If α_0, α_t and α_∞ be the angles of rotation with proper signs at the beginning, at time t and at the completion of the reaction (*i.e.*, after a very long time) respectively, then

$\alpha_0-\alpha_\infty$ is proportional to the initial concentration a

and $\alpha_0-\alpha_t$ is proportional to the amount reacted, *i.e.*, x.

Hence $$k = \frac{1}{t}\, ln \frac{\alpha_0-\alpha_\infty}{(\alpha_0-\alpha_\infty)-(\alpha_0-\alpha_t)} = \frac{2.303}{t} \log \frac{\alpha_0-\alpha_\infty}{\alpha_t-\alpha_\infty}$$

The experimental data have established the validity of this relation, *i.e.*, the first order. The reaction is carried out in presence of an acid whose concentration however remains constant throughout.

TABLE: INVERSION OF SUCROSE (25°C, 0.9 *M* HCl)

Time in min	α_t	$\alpha_t-\alpha_\infty$	$k \times 10^2$
0.0	+24.09	+34.83	—
18.0	17.73	28.47	1.117
36.8	12.40	23.14	1.112
46.0	10.02	20.76	1.113
56.0	7.80	18.54	1.113
∞	−10.74	—	—

Harcourt and Esson (1866) showed that the reduction of potassium permanganate with a great excess of oxalic acid follows the first order kinetics, the concentration of oxalic acid virtually remains unaffected.

17.7. Third Order Kinetics

Only a few third order reactions are definitely known. The simplest case of a third order reaction will be of the type,

$$3A \rightarrow \text{products}$$

So that, $$\frac{dx}{dt} = k\,(a-x)^3 \quad \text{or} \quad \frac{dx}{(a-x)^3} = kdt$$

On integration, $k = \frac{1}{2t}\left[\frac{1}{(a-x)^2} - \frac{1}{a^2}\right]$ ... (XVII.12)

The half-value period, $t_{\frac{1}{2}} = k'/a^2$ ... (XVII.13)

Most of the reactions for which a third order kinetics has been definitely confirmed, are of the type,

$$2A + B \rightarrow \text{products}$$

Of the gaseous third order reactions the following are definitely established:

(*i*) $2NO + Cl_2 = 2NOCl$ (*ii*) $2NO + H_2 = N_2O + H_2O$

(*iii*) $2NO + O_2 = 2NO_2$ (*iv*) $2NO + Br_2 = 2NOBr$ etc.

Now $\underset{a-2x}{2A} + \underset{b-x}{B} \rightarrow \text{products}$

Hence, $\frac{dx}{dt} = k(a-2x)^2(b-x)$ ... (XVII.14)

This, on integration by the method of partial fractions, gives

$$k = \frac{1}{t}\ \frac{1}{(2b-a)^2}\left[\frac{2x(2b-a)}{a(a-2x)} + ln\,\frac{b(a-2x)}{a(b-x)}\right] \quad \text{... (XVII.15)}$$

In solution, some of the well-known third order reactions are:

(*i*) $Fe(CN)_6^{3-} + 2I^- \rightarrow$ products (*iii*) $3HCNO \rightarrow [HCNO]_3$

(*ii*) $Fe^{3+} + 2I^- \rightarrow$ products

17.8. Zero Order Reactions

There are some photochemical reactions and also heterogeneously catalysed reactions, in which the reaction speed is observed to be independent of the concentration of the reactant. Hence, at any instant during the reaction, the reaction rate ($-dc/dt$) is the same. Such reactions are said to be of the '*Zero order*'.

Hence, $\frac{-dc}{dt} = k$

By integration between t = 0, and t = t, we have

$$k = \frac{C_0 - C}{t}$$

Examples of such zero order reactions are (*i*) Photochemical reaction between H_2 and Cl_2 over water (*ii*) the decomposition of HI on the surface of gold (*iii*) the decomposition of ammonia on the surface of molybdenum, etc.

17.9. Specific Reaction Rate

The velocity constant, k, used in the rate equations is equivalent to the reaction rate ($-dc/dt$) when all the reactants are at unit concentrations. The reaction rate is always expressed in moles per litre per second. The expressions for the reaction rates of different orders have different powers of concentration. The units of k must therefore be different for different orders.

For a first order reaction $k = (-dc/dt)/C$, hence the dimensions of k is moles per litre per sec/moles per litre, *i.e.*, sec^{-1}. For a second order reaction

$k = (-dc/dt)/C^2$, hence k's units would be litres mole^{-1} sec^{-1}. In general, the units for k for a reaction of nth order would be given by,

$$\frac{\text{moles per litre per sec.}}{(\text{moles per litre})^n} \; i.e., \text{ litres}^{n-1} \text{ moles}^{1-n} \text{ sec}^{-1}.$$

This rate equations for different orders of reactions are tabulated below:

Order	*Rate equation*		*units of k*
	differential	*Integrated form*	
0	$dx/dt = k$	$k = x/t$	moles litre^{-1} sec^{-1}
1	$dx/dt = k(a-x)$	$k = \frac{1}{t} . ln[a/(a-x)]$	sec^{-1}
2	$dx/dt = k(a-x)^2$	$k = \frac{1}{t} . \frac{x}{a(a-x)}$	litres mole^{-1} sec^{-1}
3	$dx/dt = k(a-x)^3$	$k = \frac{1}{2t} . \frac{2ax-x^2}{a^2(a-x)^2}$	litres^2 mole^{-2} sec^{-1}

17.10. Determination of the Order of a reaction

There are several methods for determining the order of simple reactions. In every method, it is of course essential to estimate the conc. of the reactant or the product at various time intervals.

(1) **Method of Integration:** This method has already been described in connection with the alkali hydrolysis of esters, or the inversion of cane sugar. The amounts of product (x) at different time intervals (t) are first experimentally determined. These values are then introduced into the different rate equations in their integrated forms, such as equation (XVII.5, 8, 15) etc. until a constant value for the specific reaction rate is obtained. The equation which satisfies this indicates the order of the reaction. For simple homogeneous reactions, this method of trial with rate equations is quite satisfactory and often employed. But for complex reactions, the method may lead to erroneous conclusions.

(2) **Method of Half-value Period:** The half-value period of a reaction of the nth order is

$$t_{\frac{1}{2}} = k'/a^{n-1}$$

If a and a' be the initial concentrations in two experiments of the same reaction,

then
$$\frac{t_{\frac{1}{2}}}{t'_{\frac{1}{2}}} = \left(\frac{a'}{a}\right)^{n-1}, \quad \text{or} \quad (n-1)\log\frac{a'}{a} = \log\frac{t_{\frac{1}{2}}}{t'_{\frac{1}{2}}}$$

or
$$n = 1 + \frac{\log(t_{\frac{1}{2}}/t'_{\frac{1}{2}})}{\log(a'/a)} \qquad \text{. . . (XVII.16)}$$

Plotting the concentrations against time, $t_{\frac{1}{2}}$ and $t'_{\frac{1}{2}}$ can be easily obtained, so the order n for the reaction can be calculated. Sometimes plots of $t_{\frac{1}{2}}$ *vs* $1/a$, $t_{\frac{1}{2}}$ *vs* $1/a^2$ etc. are also tried, and that which gives a linear plot would indicate the order.

(3) Differential Method: For a reaction of the *n*th order in two experiments with initial concentrations C_1 and C_2, we have,

$$\frac{-dC_1}{dt} = kC_1^n \qquad \frac{-dC_2}{dt} = kC_2^n$$

$$\text{or} \quad \log\left(\frac{-dC_1}{dt}\right) = \log k + n\log C_1; \quad \log\left(\frac{-dC_2}{dt}\right) = \log k + n\log C_2$$

$$\text{Subtracting,} \quad n = \frac{\log\left(\frac{-dC_1}{dt}\right) - \log\left(\frac{-dC_2}{dt}\right)}{\log C_1 - \log C_2} \qquad \ldots\text{(XVII.17)}$$

The procedure is to plot concentration *vs* time for two experiments with different initial concentrations. The slopes $(-dC/dt)$ at a given time interval is measured in both cases. Using these values in the above equation, n is determined.

Sometimes in the case of simple reactions, the rate $(-dC/dt)$ is obtained from the conc.-time curve, for initial 10~20% of the reaction. Then $\log(-dC/dt)$ is plotted against $\log C$ separately. The slope of the linear plot gives the value of n, the reaction order.

(4) Isolation Method: This method which was introduced by Ostwald (1902) involves an artificial simplification of the order of a reaction by using a large excess of the reactants except one. Suppose a reaction is of αth order with respect to A, and βth order with respect to B. Now if a large excess of B is used so that its concentration throughout the reaction virtually remains constant, the reaction rate will be given by

$$\frac{-dC_A}{dt} = k(C_A)^\alpha(C_B)^\beta = k'(C_A)^\alpha$$

The apparent order (α) may be determined by any of the three methods described above. The value of β can similarly be obtained by using a large excess of the reactant A. Care should be exercised in using this method, for if the reaction is a complex one excess of some components may alter the mechanism of the process and in consequence erroneous results may be obtained.

(5) Method with variation of Reaction Rate: The rate of reaction may be varied by changing the initial concentrations The determination of these rates enables the evaluation of the order as follows:

Suppose a reaction of the *n*th order is expressed as, Rate $R = kC_A^\alpha.C_B^\beta$ with initial concentrations C_A and C_B.

On doubling the concentration of A, $R_1 = k\,(2C_A)^\alpha C_B^\beta$
and on doubling the concentration of B, $R_2 = k\,C_A^\alpha\,(2C_B)^\beta$

The rates R, R_1, R_2 are experimentally determined.

$$\therefore \quad R_1/R = 2^\alpha \quad \text{and} \quad R_2/R = 2^\beta$$

$$\text{or} \quad \alpha = \frac{\log R_1/R}{\log 2} \quad \text{and} \quad \beta = \frac{\log R_2/R}{\log 2}$$

$$\therefore \quad n = \alpha + \beta = \frac{\log R_1/R + \log R_2/R}{\log 2}$$

The order is thus known.

(6) **Graphic Method:** The rate equation for a reaction of the *n*th order is

$$\frac{-dc}{dt} = kC^n$$

For a 1st order reaction; $-ln\ C = kt + \text{constant}$

For a 2nd order reaction; $\frac{1}{C} = kt + \text{constant}$

For a 3rd order reaction; $\frac{1}{C^2} = kt + \text{constant}$

The concentrations at different time intervals are determined and $-ln\ C$, $\frac{1}{C}$ or $\frac{1}{C^2}$ are plotted against time (t). The plot which will be linear will give the order of the reaction.

These methods are suitable for simple and direct reactions, where rates are simple power functions of concentrations.

17.11. Numerical Examples

Example 1. The decomposition of H_2O_2 in aqueous solution, which is of the first order, is followed by titrating equal volumes of samples of the solution with $KMnO_4$ solution as follows:

Time (min)	0	5	15	25	45
$KMnO_4$ solution (c.c.)	37.0	29.8	19.6	12.3	5.0

Calculate the rate constant of the reaction. (*Madras Univ.*)

for a first order reaction: $k = \frac{2.303}{t} \log \frac{a}{a-x}$

The titre values represent unchanged H_2O_2, *i.e.* $(a-x)$ and the initial amount '*a*' correspounds to 37.0 cc.

Hence, $$k = \frac{2.303}{5} \log \frac{37.0}{29.8} = 0.0432 \text{ min}^{-1}$$

$$k = \frac{2.303}{15} \log \frac{37.0}{19.6} = 0.0423 \text{ min}^{-1}$$

$$k = \frac{2.303}{25} \log \frac{37.0}{12.3} = 0.0406 \text{ min}^{-1}$$

$$k = \frac{2.303}{45} \log \frac{37.0}{5.0} = 0.0444 \text{ min}^{-1}$$

The average value for $k = 0.0436 \text{ min}^{-1}$.

Example 2. The decomposition of N_2O_5 in CCl_4 solution was studied by measuring the volume of O_2 produced at different time intervals, as recorded below. Show that it is a first order reaction (See sec. 17.4). (*Bombay Univ.*)

Time (min)	10	15	25	∞
V_t (oxygen)	6.30	8.95	13.50	34.75

Now the amount (a) of N_2O_5 initially is proportional to V_∞ and unchanged N_2O_5, *i.e.* $(a-x)$ is proportional to $(V_\infty - V_t)$.

Applying 1st order kinetics.

$$k = \frac{1}{t}\, ln\, \frac{a}{a-x} = \frac{2.303}{t} \log \frac{V_\infty}{V_\infty - V_t}$$

Substituting the data given

$$k = \frac{2.303}{10} \log \frac{34.75}{34.75-6.30} = 1.98 \times 10^{-2}\ \text{min}^{-1}$$

$$k = \frac{2.303}{15} \log \frac{34.75}{34.75-8.95} = 1.98 \times 10^{-2}\ \text{min}^{-1}$$

$$k = \frac{2.303}{25} \log \frac{34.75}{34.75-13.50} = 1.95 \times 10^{-2}\ \text{min}^{-1}$$

The constancy in the value of k confirms that it is a first order reaction.

Example 3. Show that for a 1st order reaction, the time required for 75% reaction is twice the time for 50% reaction (*Jadavpur Univ*).

$$t_{75\%} = \frac{2.303}{k} \log \frac{a}{a-\frac{3}{4}a} = \frac{2.303}{k} \log 4 = 2 \times \frac{2.303}{k} \log 2$$

$$t_{50\%} = \frac{2.303}{k} \log \frac{a}{a-a/2} = \frac{2.303}{k} \log 2$$

Hence, $t_{75\%} : t_{50\%} = 2 : 1$

Example 4. The first order decomposition of H_2O_2 in a suitable medium is characterised by a rate constant 3×10^{-2} min^{-1} Find the time to complete one-third of the reaction. (*Calcutta Univ.*)

For the 1st order reaction,

$$t = \frac{1}{k}\ 2.303 \log \frac{a}{a-x}$$

$$= \frac{2.303}{3 \times 10^{-2}} \log \frac{a}{a-a/3} = \frac{2.303}{3 \times 10^{-2}} \log \frac{3}{2}$$

$$= 13.5\ \text{min}$$

Example 5. In an alkaline hydrolysis of ethyl acetate by NaOH of equivalent concentration, 25 c.c. of the reaction mixtures were titrated at different time intervals against a standard acid. The litre-values are as follows:

t (min)	0	5	15	35
$(a-x)$ acid (c.c.);	16	10.24	6.13	3.41

Show that it is a second order reaction.

For a 2nd order reaction, we have

$$k = \frac{1}{t} \cdot \frac{x}{a(a-x)}$$

The initial concentration, $a = 16$ c.c. of acid solution

Substituting:

t	$(a-x)$	x	$\frac{1}{t}\cdot\frac{x}{a(a-x)} = k$ lit mol^{-1} min^{-1}
5	10.24	5.76	$k = \frac{1}{5}\cdot\frac{5.76}{16\times10.24} = 7\times10^{-3}$
15	6.13	9.87	$k = \frac{1}{15}\cdot\frac{9.87}{16\times6.13} = 6.7\times10^{-3}$
35	3.41	12.59	$k = \frac{1}{35}\cdot\frac{12.59}{16\times3.41} = 6.6\times10^{-3}$

The constancy of k confirms that the reaction is of the 2nd order.

Example 6. At 25°C, the specific rate constant for the hydrolysis of ethyl acetate by NaOH is 6.36 mol^{-1} litre min^{-1}. Starting with concentrations of base and ester as of 0.01 mole/litre. What proportion of ester will be hydrolysed in twenty minutes? (*Kerala Univ.*)

$a = b = 0.01,\quad t = 20$ min, $k = 6.36$ mol^{-1} litre min^{-1}

Let ϕ fraction be hydrolysed in 20 min.

Then, since the reaction is one of the 2nd order,

$$k = \frac{1}{t}\cdot\frac{x}{a(a-x)} = \frac{1}{t}\cdot\frac{\phi a}{a(a-a\phi)} = \frac{1}{t}\,\frac{\phi}{a(1-\phi)}$$

or
$$6.36 = \frac{1}{20}\cdot\frac{\phi}{0.01\times(1-\phi)}$$

Whence,
$$\phi = 0.56 \quad \text{or} \quad 56\%$$

Example 7. The half-value periods for the thermal decomposition of a gaseous substance are as follows with different initial pressures (P).

P (mm)	500	250
t (min)	235	950

Find the order of the reaction.

Let the reaction be of the nth order. Then

$$t_{\frac{1}{2}} = \frac{k'}{a^{n-1}} = \frac{k''}{P^{n-1}}$$

or
$$\left(\frac{P_1}{P_2}\right)^{n-1} = \frac{t_2}{t_1}\,;\ \left(\frac{500}{250}\right)^{n-1} = \frac{950}{235}$$

or
$$(n-1)\log 2 = \log\frac{950}{235},\ \text{whence n} \approx 3.$$

The reaction is of the Third order.

Example 8. The volumes of N_2 evolved from benzene diazonium chloride decomposition at different time intervals at a constant temp. are as follows:

t (min) →	0	20	50	70	∞
N_2(c.c.) →	0	10	25	35	162

Show that the reaction is of the first order with $k = 3.2\times10^{-3}$ min^{-1}

Since for a 1st order reaction,

$$k_1 = \frac{2.303}{t}\log\frac{V_\propto}{V_\alpha - t_1}, \text{ we have.}$$

$$t = 20 \text{ min}, \qquad k_1 = \frac{2.303}{20}\log\frac{162}{162-10} = 3.22 \times 10^{-3} \text{ min}^{-1}$$

$$t = 50 \text{ min}, \qquad k_1 = \frac{2.303}{50}\log\frac{162}{162-25} = 3.3 \times 10^{-3} \text{ min}^{-1}$$

$$t = 70 \text{ min}, \qquad k_1 = \frac{2.303}{70}\log\frac{162}{162-35} = 3.25 \times 10^{-3} \text{ min}^{-1}$$

Example 9. $FeCl_3$ is reduced by $SnCl_2$. Equivalent amounts of the two reactants were taken at a const. temp. with conc. $C = 0.0625$. The reaction was followed by withdrawing same amount from time to time and run into $HgCl_2$ soln to remove excess $SnCl_2$. The ferrous chloride was then estimated against standard dichromate soln. The readings are

t (min) →	1	3	7	40
titre x →	0.01434	0.02664	0.03612	0.0506

The reaction is $2FeCl_3 + SnCl_2 = 2FeCl_2 + SnCl_4$

and $$k = \frac{1}{2t}\left[\frac{1}{(a-x)^2} - \frac{1}{a^2}\right] \text{ for a third order reaction.}$$

Now

$$t = 1, \qquad k = \frac{1}{2\times1}\left[\frac{1}{(0.04816)^2} - \frac{1}{(0.0625)^2}\right] = 87$$

$$t = 3 \qquad k = \frac{1}{2\times3}\left[\frac{1}{(0.0359)^2} - \frac{1}{(0.0625)^2}\right] = 87$$

$$t = 40 \qquad k = \frac{1}{2\times40}\left[\frac{1}{(0.0119)^2} - \frac{1}{(0.0625)^2}\right] = 85$$

Hence the reaction is of the third order.

SIMULTANEOUS REACTIONS

The equations for rate constants which have been developed earlier apply to only simple and straight forward reactions. But often the reactant or the products undergo more changes than the one considered. These are called *simultaneous reactions*. The simultaneous reactions may generally be of three classes; (*i*) *Opposing reactions* (*ii*) *Consecutive reactions* (*iii*) *parallel reactions.*

17.12. Opposing Reactions

In a reversible process, if the equilibrium is far away from one end, then the reaction may be found to follow a simple reaction rate at least in the beginning of the reaction, the very slow reverse process being ignored. But when the reaction rates are appreciable for both the forward and the reverse processes, the kinetics must take into consideration both the processes. The simplest case is when both the forward and the reverse reactions are of the first order, as

$$\underset{(a-x)}{\mathrm{A}} \underset{k_2}{\overset{k_1}{\rightleftharpoons}} \underset{x}{\mathrm{B}},$$

k_1 and k_2 being the specific reaction rates in the two opposite directions. Starting with pure A of concentration a, let x be the concentration of B after time t, then

$$\frac{dx}{dt} = k_1(a-x) - k_2x = k_1a - (k_1+k_2)x$$

The rate constants, k_1 and k_2 can be ascertained from this equation with a knowledge of the eqm. constant ($K = k_1/k_2$) of the reaction.

Examples of such reversible reactions:
(*i*) hydroxy butyric acid ⇄ lactone
(*ii*) Cis-trans isomerism of styryl cyanide
(*iii*) ammon. thiocyanate to thiourea
(*iv*) hydrolysis of esters

17.13. Consecutive Reactions

Consecutive reactions may be represented as:

$$\mathrm{A} \xrightarrow{k_1} \mathrm{B} \xrightarrow{k_2} \mathrm{C},$$

that is, the reactions proceed from reactants to products through one or more intermediate stages. The overall reaction is a result of several consecutive steps. Every stage, has its own reaction rate and velocity constant. The simplest case is one in which there are only two consecutive stages and the two reactions are of the 1st order with specific reaction rates k_1 and k_2.

Suppose c_0 is the initial concentration of A, and let c_1, c_2 and c_3 denote the concentrations of A, B and C respectively at any time t. We have, therefore,

$$c_0 = c_1 + c_2 + c_3$$

and, the rate of disappearance of A, $-\dfrac{dc_1}{dt} = k_1c_1$

Hence, $$c_1 = c_0e^{-k_1t} \qquad \text{. . . (A)}$$

Since the rate of formation of B is given by k_1c_1 and the rate of decomposition of B into C is given by k_2c_2, the rate at which B accumulates in the system is

$$\frac{dc_2}{dt} = k_1c_1 - k_2c_2 \qquad \text{. . . (B)}$$

The rate constants can be computed by solving the differential equations (A) and (B). Examples of consecutive reactions:

(*i*) The thermal decomposition of acetone.

$$(CH_3)_2CO \rightarrow CH_2{=}CO + CH_4$$
$$\hookrightarrow \tfrac{1}{2}C_2H_4 + CO$$

(*ii*) The decomposition of demethyl ether,

$$(CH_3)_2O \rightarrow CH_4 + HCHO$$
$$\hookrightarrow CO + H_2$$

(*iii*) The acid hydrolysis of dibasic acid esters,

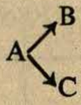
$$\begin{array}{l} CH_2.COOEt \\ | \\ CH_2.COOEt \end{array} \xrightarrow[-EtOH]{+H_2O} \begin{array}{l} CH_2COOEt \\ | \\ CH_2COOH \end{array} \xrightarrow[-EtOH]{+H_2O} \begin{array}{l} CH_2COOH \\ | \\ CH_2COOH \end{array}$$

(*iv*) Oxidation of HI by H_2O_2,

$$H_2O_2 + I^- \rightarrow H_2O + OI^-$$
$$OI^- + H^+ \rightarrow HOI$$
$$HOI + H^+ + I^- \rightarrow H_2O + I_2$$
$$\overline{H_2O_2 + 2H^+ + 2I^- \rightarrow 2H_2O + I_2}$$

17.14. Side Reactions or Parallel Reactions

Sometimes a reactant can undergo changes in more than one way. These are termed *parallel* or *side reactions.*



Let *a* be the initial concentration of A and *x* be the amount disappeared in time *t*, partly as B and partly as C. The amount of A present after the time interval *t* is $(a-x)$. If k_1 and k_2 be the specific rate constants of the two reactions, then assuming both the reactions to be of the 1st order, we have

$$\frac{dx}{dt} = k_1(a-x) + k_2(a-x) = (k_1 + k_2)(a-x)$$

Integrating, $\frac{1}{t} \ln \frac{a}{a-x} = k_1 + k_2$ ...(C)

Again, if w_B and w_C be the quantities of B and C formed (and estimated) after any given time or at eqm. then

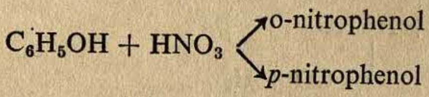
$$\frac{w_B}{w_C} = \frac{\text{Rate of formation of B}}{\text{Rate of formation of C}} = \frac{k_1(a-x)}{k_2(a-x)} = \frac{k_1}{k_2} \qquad \text{...(D)}$$

The value of $(k_1 + k_2)$ is known from (C) and that of k_1/k_2 from (D). Hence, both the rate constants are known. The equation (D) is applicable only when both the reactions are of the same order. This is known as 'Wegscheider test'.

Examples: (*a*) Wegscheider had shown that when HCl was added to cinchonine, ordinary hydrochloride and its isomer were formed. The amounts of the two were in constant ratio independent of the time chosen for measurement,

$$\begin{array}{l} \text{Cinchonine} + HCl \\ (C_{19}H_{22}ON_2) \end{array} \begin{array}{l} \nearrow \text{cinchonine hydrochloride} \\ \searrow \text{isomeric cinchonine hydrochloride} \end{array}$$

(*b*) Nitration of phenol (both reactions are of second order),



$$C_6H_5OH + HNO_3 \begin{cases} \nearrow \text{o-nitrophenol} \\ \searrow p\text{-nitrophenol} \end{cases}$$

(*c*) Decomposition of ethanol vapour,

$$C_2H_5OH \rightarrow C_2H_4 + H_2O \quad ; \quad C_2H_5OH \rightarrow CH_3CHO + H_2$$

THEORIES FOR RATES OF REACTIONS

17.15. Temperature and Reaction Rates: The Arrhenius Equation

Temperature has a profound influence on the reaction velocity. In homogeneous thermal reactions, for every ten-degree rise in temperature, the velocity of reaction is doubled or trebled. The ratio, called *temperature coefficient*, is $\frac{k_{t+10}}{k_t} \approx 2$ to 3. The enhancement of reaction rate is found with reactions in gaseous as well as in solution phases. Some typical data are given below:

TABLE: REACTION RATES AT DIFFERENT TEMPERATURES

(*A*) *Decomposition of* N_2O_5 (gas)		(*B*) *Reaction in alcoholic solution* $CH_3I + C_2H_5ONa \rightarrow CH_3OC_2H_5$	
Temp°C	$k \times 10^4$ *sec*$^{-1}$	*Temp.*°C	$k \times 10^5$ *litre/mole-sec.*
25	0.34	0	5.6
35	1.35	6	11.8
45	4.98	12	24.5
55	15.0	24	100
65	48.7	30	208

Arrhenius (1889) showed that the velocity constant (k) of a chemical process increases exponentially with temperature for a large number of reactions. It was observed that $\log k$ plotted against $1/T$ gives a straight line. He, therefore suggested *empirically* the relation as

$$\frac{d \ln k}{dT} = \frac{E}{RT^2} \qquad \text{...(XVII.18)}$$

Integrating, $$k = A\,e^{-E/RT} \; ; \; (A, \text{constant}) \qquad \text{...(XVII.19)}$$

or $$\log k = \frac{-E}{2.303R} \cdot \frac{1}{T} + \log A \qquad \text{...(XVII.20)}$$

These are the different forms of *Arrhenius Equation*.

'A' is called the **frequency factor** or the **pre-exponential factor** and 'E' is called the **activation energy** of the reaction. These two have definite values for a given reaction.

If k and k' denote the rate constants at two temperatures T and T', then, from eqn. (XVII. 20),

$$\log k = -\frac{E}{2.303R}\cdot\frac{1}{T} + \log A; \quad \text{and} \quad \log k' = -\frac{E}{2.303R}\cdot\frac{1}{T'} + \log A$$

or
$$\log\frac{k}{k'} = \frac{-E}{2.303R}\left[\frac{T'-T}{TT'}\right] \qquad \ldots \text{(XVII.21)}$$

Hence, the activation energy (E) can be evaluated by measuring the velocity constant of the reaction at two temperatures.

Activation energy and Heat of Reaction: Suppose k_1 and k_2 are the velocity constants in the two opposite directions of a reversible process at temp T. From eqn. (XVII.20),

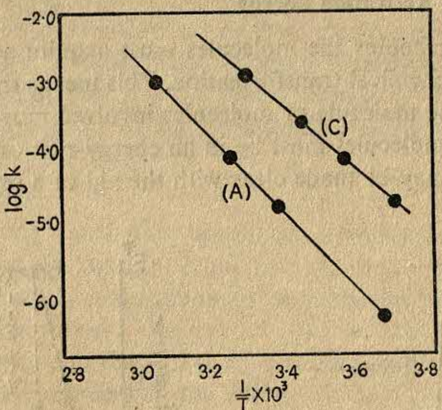


Fig. XVII.2.

$$ln\, k_1 = \frac{-E_1}{RT} + z_1 \text{(constant)}$$

and
$$ln\, k_2 = \frac{-E_2}{RT} + z_2 \text{(constant)}$$

Subtracting,
$$ln\,\frac{k_1}{k_2} = \frac{(E_2-E_1)}{RT} + z$$

But $\frac{k_1}{k_2} = K$, equilibrium constant of the reaction, and $(z_1-z_2) = z$, constant.

Hence, $ln\, K = \frac{E_2-E_1}{RT} + z$

where E_1 and E_2 are the activation energies of the two opposite processes.

Hence,
$$\frac{d\,ln\,K}{dT} = -\frac{(E_2-E_1)}{RT^2} = \frac{E_1-E_2}{RT^2} \qquad \ldots \text{(XVII.22)}$$

But from van't Hoff isochore, $\frac{d \ln K}{dT} = \frac{\triangle H}{RT^2}$

where $\triangle H$ is the heat-change of the chemical process.

Comparing,
$$\triangle H = E_1 - E_2 \qquad \ldots \text{(XVII.23)}$$

It is obvious that the activation energy (E) in the Arrhenius equation must have units of energy. *The heat of reaction of a process is the difference in the energies of activation of the two opposing changes.*

Example 8. The rate constant of a certain reaction is found to be doubled when temperature is raised from 27°C to 37°C. What is the activation energy? (*Cal. Univ.*).

Applying eqn. (XVII.21),

$$\log \frac{k}{2k} = -\frac{E}{2.303R}\left(\frac{1}{300} - \frac{1}{310}\right) = \frac{-E}{2 \times 2.303} \times \frac{10}{300 \times 310}$$

or $-E = \log(0.5) \times 2 \times 2.303 \times 30 \times 310$ or $E = 12.89$ kcal

17.16. Significance of Activation Energy

According to Arrhenius the molecules must acquire a certain energy before they would undergo chemical transformation. This means that before the chemical reaction can occur the molecule or molecules involved must be raised to a higher energy level *i.e.*, the molecules must be in an energy-rich or activated state before they can react. This may be made clear with the aid of a schematic diagram as in Fig. XVII.3.

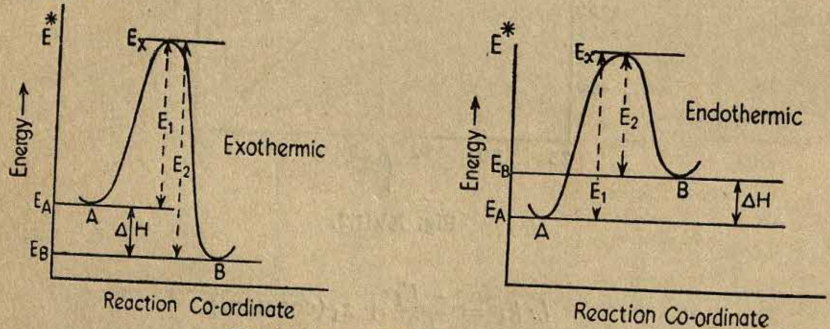


Fig. XVII.3. Activation energy

The average energy of the reactant is represented by E_A and that of the resultant by E_B. But even if E_A is greater than E_B the reactant A will not be straightway transformed to the product B. There is a minimum energy level for the reaction denoted by E_X to which the reactant molecule must be raised in order to enable it to undergo the chemical change. The excess or additional energy ($E_X - E_A$) which the reactant must acquire in order to undergo transformation is the activation energy, E_1. Molecules, having energy E_X or above, are said to be in *activated state* and such molecules only are fit for chemical reaction. This idea of the activated state (or activated complex formed from reactants) has been qualitatively presented in Fig. XVII.3.

The acquisition of the energy of activation by the reactant molecules leads to the change in their structural orientations, their internal vibrations, their internuclear distances etc. and even a transient association may take place. Finally the activated molecules suffer transformation. It is obvious that higher the threshhold energy level E_X, greater is the activation energy and hence lesser will be the number of activated molecules.

After the chemical transformation, the products will have the average energy E_B. Hence an amount of energy $(E_X - E_B) = E_2$ will be given out. If $E_2 > E_1$, the reaction is evidently exothermic, whereas if $E_2 < E_1$, the reaction is endothermic (see. Fig. XVII.3).

Moreover, if the reverse reaction B → A is followed, the molecules of B must reach the level E_X by acquiring energy E_2 and thus be activated to be transformed into A molecules. Then, on reaction, the excess energy E_1 will be given up by the activated species.

This concept that the molecules must possess the activation energy before they can undergo the chemical change has now been universally accepted for all reactions. It is now necessary to find out how the activation of the molecules is realised and how the molecules behave during the transformation. In other words, a probe into the molecular mechanism of reactions is necessary. Attempts in the elucidation of the mechanism led to two theories, namely (*i*) the collision theory and (*ii*) the transition state theory. We shall now briefly mention these two theories.

17.17. The Collision Theory

Molecules will not react unless they are raised to the activated state. According to the collision theory, the reactant molecules, say A and B, in order to react, must collide and thereby acquire enough energy for them to be activated. This is the basic postulate of this theory. The rate of reaction then must depend upon the number of collisions per unit time between the reactant molecules. It is obvious that every collision will not succeed in the activation of reactants and lead to reaction. Only those collisions in which the activation energy level is reached are fruitful and these would lead to the chemical change. The high energy available at the moment of impact will help to effect the necessary rearrangement of the atoms in the molecules leading to the reaction. The collision theory explains satisfactorily the gaseous reactions, especially the bimolecular ones.

The number of binary collisions Z per c.c. per second in a gas of unit concentration can be easily calculated from the kinetic theory. A fraction of theses Z collisions will raise the molecules to the activated state, other collisions having lesser energy would be infructuous. The rate of reaction will be given by the number of fruitful collisions.

Again, all the molecules in a gas do not possess the same energy; the energy is distributed amongst the molecules according to Maxwell-Boltzmann Law. It has been shown that the fraction of the total number of molecules (n_0) possessing an energy ϵ (or higher) above the average energy value at temperature T, is given by

$$\frac{n}{n_0} = e^{-\epsilon/RT}, \text{ (called the Boltzmann factor).}$$

Hence the number of effective collisions in which activated molecules (having energy E above the average) will be involved will be given by $Z.e^{-E/RT}$

Hence, the rate of reaction is $\frac{-dn}{dt} = Z..e^{-E/RT}$. per c.c. per sec.

Using proper units, the rate can be expressed in moles/litre. This rate is found to be the same as that of the Arrhenius equation, the collision number Z corresponds to the pre-exponential factor, A.

To illustrate: For the reaction $2HI \rightarrow H_2 + I_2$

$k = 3.5 \times 10^{-7}$ mole/litre sec^{-1} (from experiment)

and $k = 5.2 \times 10^{-7}$ mole/litre sec^{-1} (calculated from theory)

In many other gaseous reactions, the concordance between the results from collision theory and the experiment is quite satisfactory.

17.18. The Transition-State Theory

The *transition-state theory*, also known as the *absolute reaction-rate theory* was developed in 1935 by Eyring and by Polanyi. It has been conceived in this theory that the reactant molecules first form an energy-rich intermediate complex, which then breaks up into the product molecules. Two or more reactant molecules, possessing sufficient energy, come close together when a rearrangement of their internal bonds and energy occurs. As a result, they are transformed into an *activated complex* often by association through new bonds. If it be a unimolecular reaction, the reactant molecule may produce the activated complex by rearrangement of atoms and redistribution of energy. The activated complex, though unstable and has a transient existence, is to be considered as a definite molecule with independent entity. The activated complex then breaks up to produce the resultants.

$$\text{Reactants} \rightleftharpoons \text{activated complex} \rightarrow \text{Products}$$

In considering the HI-dissociation, we may visualise it as follows:

$$\begin{array}{ccccccccccc} H-I & & H-I & & H\cdots\cdots I & & H & & I & & \\ & \rightarrow & \vdots \quad \vdots & \rightarrow & \vdots \qquad \vdots & \rightarrow & | & + & | & \rightarrow & H_2 + I_2 \\ H-I & & H-I & & H\cdots\cdots I & & H & & I & & \end{array}$$

As to the activated complex, the following postulates are accepted:

(*a*) The activated complex is regarded as a separate entity, and it is always in equilibrium with the reactant molecules. If C_A and C_B be the concentration of reactants and $C^{\ddagger}$ is the concentration of the activated complex (X) in the reaction,

$$(i)\ A + B \rightleftharpoons X \quad ; \quad (ii)\ X \rightarrow \text{Products}$$

the eqm. const. $$K^{\ddagger} = \frac{C^{\ddagger}}{C\ .\ C_B}$$

The suffix (‡) refers to the activated complex.

(*b*) The activation energy (E) of the reaction is the additional energy which the reactant molecules acquire to form the activated complex (X).

(*c*) The activated complex must have one of its vibrational degrees of freedom which would be quite unstable. This vibration is responsible for disrupting the complex into the products. The vibration happens to have a large enough amplitude to break open the complex.

On this basis it can be shown that the velocity constant (k_1) of a reaction would be

$$k_1 = \frac{kT}{h} K^{\ddagger} \qquad \ldots \text{(A)}$$

where k = Boltzmann constant, h = Planck constant. The eqm. constant, $K^{\ddagger}$ is evaluated thermodynamically. The velocity constant k_1 calculated from eqn (A) above is often confirmed by experiment.

CHAIN REACTIONS

17.19. Chain Reactions

The reactions which have so far been considered are explained in terms of mechanism of their taking place either in a single step or in a series of intermediate steps. The intermediate steps ultimately lead to the products. There is however a group of reactions which proceed by a long series of self-repeating steps. When the final product is formed, the active intermediate species is regenerated to carry on the reaction. Such reactions are called *chain reactions*.

In 1906 Bodenstein found that the reaction between H_2 and Br_2 was not a simple bimolecular one like that between H_2 and I_2. The reaction was a complicated one and appeared to follow a kinetics expressed by the relation,

$$\frac{dC_{\mathrm{HBr}}}{dt} = \frac{kC_{\mathrm{H_2}} \,.\, C^{\frac{1}{2}}_{\mathrm{Br_2}}}{1 + k'\, C_{\mathrm{HBr}}/C_{\mathrm{Br_2}}} \qquad \ldots \text{(XVII.24)}$$

No explanation of such results was available until in 1920 Christiansen, Herzfeld and Polanyi all independently proposed a scheme of self-propagating steps in the formation of HBr. At the first stage, molecules of bromine are dissociated into atoms. The Br-atoms then carry on the process in the following way:

			Rate constants
Chain initiation	(1) Br_2	$\rightarrow$ 2Br	k_1
Chain propagation	(2) $Br + H_2$	$\rightarrow$ HBr + H	k_2
	(3) $H + Br_2$	$\rightarrow$ HBr + Br	k_3
Chain inhibition	(4) H + HBr	$\rightarrow$ H_2 + Br	k_4
Chain-break	(5) Br + Br	$\rightarrow$ Br_2	k_5

Evidently the process is initiated with formation of Br-atoms in (1). A Br-atom then leads to the formation of HBr through reactions (2) and (3). Two molecules of HBr are formed and the Br-atom is regenerated to continue the cycle. These self-propagating steps are likely to continue endlessly through repeated generation of chains of Br-atoms and H-atoms. Thus for any initial Br-atom, a large number of HBr would result. Only sometimes a chance collision between H and HBr (4) inhibits the process or when two Br-atoms come together to unite into a Br_2-molecule, the chain is broken or stopped. In fact in all chain reactions, three stages are involved: (*i*) the initiation of the chain (*ii*) the propagation of the chain and (*iii*) the breaking of the chain.

This mechanism for the H_2-Br_2 reaction completely supported the experimental results (eqn XVII.24). The chain is continued through atomic hydrogen and atomic bromine. Other such atom-chain reactions are also known, for example: $CO + Cl_2 \rightarrow COCl_2$. It has been found to be a chain reaction, expressed as:

$$\begin{gathered} Cl_2 \rightarrow Cl + Cl \\ Cl + CO \rightarrow COCl \\ COCl + Cl_2 \rightarrow COCl_2 + Cl \\ 2Cl \rightarrow Cl_2 \end{gathered}$$

The rate of formation of phosgene is given by

$$\frac{dC_{\mathrm{COCl_2}}}{dt} = kC_{\mathrm{CO}} \cdot C_{\mathrm{Cl_2}}^{\frac{1}{2}}$$

which supports the experimental observation.

Many other reactions, specially the organic ones, are now known to occur through chains continued by radicals instead of atoms. As an illustration, we may cite the thermal decomposition of acetaldehyde.

The chain mechanism is initiated by the formation of a methyl radical which follows the steps as:

			Rate constant
Chain initiation	(*i*) CH_3CHO	$\rightarrow CH_3 + CHO$	k_1
Chain propagation	(*ii*) $CH_3 + CH_3CHO$	$\rightarrow CH_4 + CH_3CO$	k_2
	(*iii*) CH_3CO	$\rightarrow CO + CH_3$	k_3
Chain breaking	(*iv*) $CH_3 + CH_3$	$\rightarrow C_2H_6$	k_4

The rate of decomposition is given by $\frac{dC_{\mathrm{CH_4}}}{dt} = kC^{3/2}_{\mathrm{CH_3CHO}}$

EXERCISES

I

1. Explain and illustrate: (*i*) Order of a reaction (*ii*) molecularity of a reaction. What is the order of the reaction for thermal dissociation of acetaldehyde? Name a zero-order reaction.

2. What is meant by specific rate constant? In what unit it is expressed? How is rate constant affected by change in concentration and temperature?

3. What is 'order of a reaction'? Describe some important methods for determining the order of a reaction. (*Cal. Univ.*)

4. What is the meaning of 'half-value period'? Show that the plot of half-value periods against concentration will be linear in the case of 1st order reaction.

5. Derive the kinetic equation for a first order reaction. What does the rate constant signify? State if the half-value period of such a reaction would depend upon the concentration. (*Cal. Univ.*)

6. (*a*) What do you understand by the term 'Psuedo Unimolecular reactions'. Give two examples. (*b*) Describe a method for the determination of rate of hydrolysis of an ester. (*Punjabi* Univ.)

7. (*a*) Deduce an expression for the rate constant of a second order reaction. What will be the half-life of such a reaction involving only one reactant? (b) Give an outline of the method you would take to study the rate of hydrolysis of ethyl acetate with NaOH.

8. How would you determine experimentally the order of the following reactions: (*i*) Inversion of cane sugar solution in presence of an acid (*ii*) Decomposition of H_2O_2?

9. Discuss the influence of temperature on the velocity of a reaction. State and explain Arrhenius equation in this connection. Why, at a given temperature, some reactions are slow but others are fast?

10. What is meant by 'activation energy'? How can you estimate it? How is it related to the heat of reaction?

11. Write explantory notes on: (*a*) temperature coefficient of a reaction (*b*) consecutive reactions (*c*) side reactions (*d*) energy of activation.

12. What are chain reactions? Cite one example of an inorganic reaction and one of an organic reaction which occur through chain mechanism, giving the chains involved.

13. Critically examine the following statements:

(*a*) The half-life of a first order reaction is proportional to the initial concentration of the reactant.

(*b*) The activation energy level of the forward and the backward reaction is the same. Hence the activation energies of the two opposite reversible processes are equal.

(*c*) The synthesis of ammonia is an exothermic process, its rate of formation will decrease with rise in temperature.

II

1. From the data given below, show that the decomposition of H_2O_2 in aqueous solution is of the 1st order.

t (min)	0	5	10	20	30
N (c.c.)	46.7	37.7	29.8	19.6	12.3

where N = volume $KMnO_4$ solution required to titrate a definite volume of H_2O_2 solution. (*Punjab Univ.*) [Ans. k (average) = 0.0441 min^{-1}]

2. The optical rotation of a sucrose solution in 0.9 M HCl at different time intervals are

t (min)	0	7.18	27.05	∞
Rotation (degree)	+24.09	+21.4	+15.0	−10.74

Show that the reaction is of the 1st order. [Ans. k = 0.011 min^{-1}]

3. The conversion of *N*-chloroacetanitide (*A*) into *p*-chloro acetanilide (*B*) was followed by adding KI-solution and titrating the liberated iodine with standard $Na_2S_2O_3$ solution. KI reacts with *A* only.

Time (hours)	0	1	2	3	4	6
$Na_2S_2O_3$ Soln (c.c.)	49.3	35.6	25.75	18.5	14.0	7.3

Calculate the 1st order rate constant per second. [Ans. $8.9 \times 10^{-5}\ \text{sec}^{-1}$]

4. For a reaction $A \rightarrow$ Products, the following data were obtained at 25°C in which C_A = Conc. of A in moles litre^{-1} present at time t.

t (sec)	0	5	10	20	30
C_A	0.461	0.371	0.298	0.196	0.123

Show by substitution and by graphical method that the reaction is of the 1st order. Calculate $t_{\frac{1}{2}}$. (*Lucknow Univ.*) [Ans. $t_{\frac{1}{2}}$ = 15.96 sec]

5. The reaction $SO_2Cl_2 \rightarrow SO_2 + Cl_2$ is a first order reaction with $k = 3.2 \times 10^{-5}$ sec^{-1}. What percentage of SO_2Cl_2 will be decomposed in heating this gas for 90 minutes? (*Gauhati Univ.*). [Ans. 84%]

6. Show that in case of a unimolecular reaction, the time required for 99.9% reaction to take place is ten times that required for half of the reaction.

7. A first order reaction is 25% complete at the end of 20 minutes. How long will it take to complete 75%? [Ans. 96.12 min]

8. 75% of a reaction of the 1st order was completed in 32 minutes. When was half completed? [Ans. 16 min]

9. For the second order reaction; $CH_3COOEt + OH^- \rightarrow CH_3COO^- + EtOH$, $k = 6.21 \times 10^{-3}$ lit mol^{-1} sec^{-1}. Calculate time for 90% hydrolysis when initial concentrations are 0.05 M for both. [Ans. 2.9×10^4 sec]

10. A mole of ethyl acetate was hydrolysed with a mole of NaOH when the concentrations fell according to the following data:

t (min)	0	4	6	10	15	20
$(a-x)$	8.04	5.3	4.58	3.50	2.74	2.22

Calculate k. (*Udaipur Univ.*) [Ans. $k = 1.613 \times 10^{-2}$]

11. For a reaction, the values of the rate constants at 25°C and 65°C were 3.46×10^{-5} and 4.81×10^{-3} respectively. Calculate the energy of activation (*Punjabi Univ.*) [Ans. 2.49 kcal]

12. In the thermal decomposition of a gaseous substance the time for the decomposition of half the reactants was 105 min when the initial pressure was 750 mm and 950 min when the initial pressure was 250 mm. Find the order of the reaction. (*Kurukshetra Univ.*) [Ans. 3rd order]

13. In the reduction of NO, 5% of the reaction was complete in 140 seconds when initial pressure was 258 mm and in 224 seconds when initial pressure was 202 mm. Find the order of the reaction. (*Punjabi Univ.*) [Ans. 3rd order]

14. At 25°C, the half-life period of the decomposition of N_2O_5 is 5.7 hours and is independent of the initial pressure. Calculate the specific reaction rate and time required for the reaction to go to 90% decomposition. (*Viswabharati*) [Ans. 0.122 hr^{-1}, 18.9 hrs]

15. Half-change time of decomposition of a compound was found to be 50 min. When the concentration to start with was halved, the $t_{\frac{1}{2}}$ became 100 minutes. What is the order of the reaction? (*Delhi Univ.*) [Ans. 2nd order]

CHAPTER 18

CATALYSIS

18.1. Catalysts and Catalysis

It is often seen that the speed of a reaction is altered by the presence of a foreign substance which remains unchanged at the end of the reaction. Such substances are called *catalysts*, for example, MnO_2 used in the decomposition of $KClO_3$. To define: *A catalyst is a substance which alters the speed of a reaction itself remaining unaltered in mass and chemical composition.* The phenomenon is called *Catalysis.* Thus, NO acts as a catalyst in the oxidation of SO_2 to SO_3; OH^- accelerates the decomposition rate of H_2O_2, etc.

Positive and Negative Catalysis: (*a*) when the speed of a reaction is enhanced by the presence of a catalyst, it is a case of *positive catalysis*. For example:

(*i*) Iron is a positive catalyst in the synthesis of ammonia
(*ii*) Cu^{++} ion is a positive catalyst in the autooxidation of Na_2SO_3 solution
(*iii*) H^+ ion accelerates the hydrolysis of esters, etc. etc.

(*b*) Sometimes the speed of a reaction is slowed down or even stopped by a catalyst, it is *negative catalysis*. For example:

(*i*) H^+ ion retards the rate of decomposition of H_2O_2
(*ii*) glycerol retards the rate of oxidation of sulphite solution by air
(*iii*) alcohol retards the rate of oxidation of chloroform to phosgene etc.

Now-a-days many authors use the term 'Catalysis' only to mean enhancement of the speed of reactions, *i.e.*, positive catalysis. The behaviour and function of the negative catalysts do not often fully satisfy the strict requirement of the definition of catalysts, since the so-called negative catalysts are sometimes used up or changed permanently in the process. The negative catalysts are now commonly mentioned as *inhibitors*.

18.2. Characteristic Features of Catalysis

The catalytic reactions are characterised by the following criteria:

(*i*) *The catalyst remains unchanged in mass and in chemical composition at the end of the reaction.* But its physical state may be modified profoundly. Bright Pt-strips used as catalyst in the formation of SO_3 from SO_2 is transformed into Pt-black during the process.

(*ii*) *A very minute quantity of a catalyst can produce an appreciable effect on the speed of a reaction.* Titoff showed that Cu^{++} at a conc. of 10^{-12} gm-ions/litre would cause an appreciable rise in the rate of oxidation of $NaHSO_3$-solution by air. Small amounts of enzyme catalyses the fermentation of enormous quantities of sugar.

(*iii*) *The catalyst cannot start a reaction but only increases or decreases its speed.* In fact, the catalyst functions as an agent to find out an alternative path for the process.

(*iv*) *The catalyst has no effect on the final state of equilibrium.* In a chemical process, say A→B, the free energy change $\triangle G$ will always be the same and independent of the path of transformation and $\triangle G^\circ = RT \ln K$. Since the catalyst is reproduced at the end, it does not contribute any energy to the system. Hence $\triangle G^\circ$ will be the same whether the reaction is fast or slow. Therefore, K shall not alter. The equilibrium constant will be unaffected by the presence of a catalyst.

Now eqm. constant $K = k_1/k_2$, *i.e.* the ratio of the velocity constants of the forward and the backward reactions, would remain constant inspite of the presence of the catalyst. It is obvious that *a catalyst influences the forward and the backward reactions to the same extent.* For example, in the reversible process,

$$CH_3COOEt + H_2O \underset{[H^+]}{\overset{[H^+]}{\rightleftharpoons}} CH_3COOH + EtOH$$

the catalyst H^+-ion accelerates both the hydrolysis of the ester as also the esterification of the acid.

It is convenient to divide the catalysed reactions into two groups, namely, homogeneous and heterogeneous. In homogeneous catalysis, the catalyst forms a single phase with the reactants, such as nitric-oxide in oxidation of SO_2 in the chamber process, or acids catalysing the hydrolysis of esters. In heterogeneous catalysis, the catalyst and the reactants constitute separate phases and often the surface or interface is responsible for the catalytic effect, such as, nickel in the hydrogenation of unstaturated oils.

18.3 Homogeneous Catalysis

Many homogeneously catalysed reactions have been studied in the gas-phase and in the liquid-phase. Common examples of such catalysis in gas-phase are the catalytic effect of nitric oxide in the oxidation of carbon monoxide to dioxide or the decomposition of nitrous oxide to nitrogen and oxygen, iodine vapour catalysing the decomposition of ethers or acetaldehyde vapours, etc. The reaction rates in homogeneously catalysed reactions are invariably found to be proportional to the concentration of the catalyst. The theory for the the mechanism of the homogeneously catalysed reactions can be understood from the following:

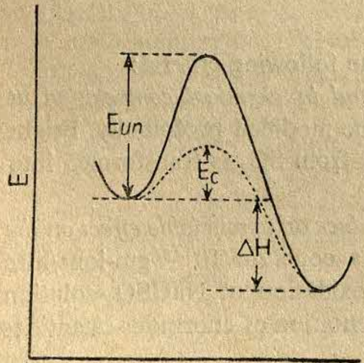


Fig. XVIII.1 Activation energies of uncatalysed (E_{un}) and catalysed (E_c) reaction.

Although the catalyst is received back entirely at the end of the reaction, yet it does actively participate in the reaction process. In enhancing the speed of a reaction, the catalyst does combine with a reactant or an intermediate forming a complex which subsequently breaks up to yield the products along with the catalyst itself. The reactant with which the catalyst combines is often mentioned as a **substrate**. The catalyst really provides an alternative path for the transformation in which the required activation energy is less (Fig. XVIII.1). Lesser activation energy permits larger amount of reaction in a given time. The rate, of course, depends upon the catalyst-concentration. For example, the uncatalysed decomposition of acetaldehyde is found to have an activation energy of 45500 cal. When it is catalysed with I_2-vapour, the reaction is a bimolecular one with the lesser activation energy of 32000 cal.

The mechanism for the decomposition of CH_3CHO with iodine as catalyst is as follows:

$$\begin{array}{llll}
(a) & CH_3CHO + I_2 & \rightarrow CH_3I + HI + CO & \text{(slow)} \\
(b) & CH_3I + HI & \rightarrow CH_4 + I_2 & \text{(fast)} \\
\hline
 & CH_3CHO & \rightarrow CH_4 + CO &
\end{array}$$

The presence of iodine enhances the speed several thousand times. The reaction rate is governed by the relatively slower stage (*a*), when the activation energy is 32000 cal, whereas the activation energy of uncatalysed process is 45500 cal.

The rate, $$\frac{dx}{dt} = k_c . C_{I_2}\, C_{aldehyde} = k\ C_{aldehyde}$$

where k_c is the catalytic coefficient for the catalyst iodine for the said reaction.

In general, a homogeneously catalysed reaction is explained in the following way:

$$(i)\ S + C \underset{k_2}{\overset{k_1}{\rightleftharpoons}} X\,; \qquad (ii)\ X \overset{k_3}{\rightarrow} P + C$$

where S is substrate, C catalyst, P product and X the intermediate compound.

The rate of formation of the product, $\frac{dC_P}{dt} = k_3 C_X$

The concentration of the intermediate C_X is usually quite-small. When the reaction proceeds smoothly and steadily, the rate at which the intermediate X is formed is the same at which it disappears into products, *i.e.* the conc. of X in the system is small and constant, hence $\frac{dC_X}{dt} = 0$. This is often called the *steady-state principle*.

The rate of formation of X $= k_1 C_S . C_C$

The rate of disappearance of X $= k_2 C_X + k_3 C_X$. From the above principle, the two rates are equal.

$$\therefore \qquad k_1 C_S . C_C = k_2 C_X + k_3 C_X$$

$$\text{or} \qquad C_X = k_1 C_S . C_C / (k_2 + k_3)$$

Hence, the reaction rate, $$\frac{dC_P}{dt} = k_3 C_X = k_3 . \frac{k_1 C_S C_C}{k_2 + k_3} = k_C . C_C C_S$$

It shows that in homogeneous catalysis, the rate depends on the catalyst-concentration (C_C). For a given concentration of the catalyst,

$$\frac{dC_P}{dt} = k'C_S$$

where $k' = k_C C_C$. The constant k_C is known as the *catalytic coefficient of* the catalyst.

Some illustrations of the homogeneously catalysed reactions are appended below.

(*i*) Oxidation of SO_2 catalysed with NO,

$$\begin{array}{rcl} O_2 + 2NO &=& 2NO_2 \\ 2SO_2 + 2NO_2 &=& 2SO_3 + 2NO \\ \hline 2SO_2 + O_2 &=& 2SO_3 \end{array}$$

the existence of NO_2 being experimentally confirmed.

Homogeneous catalysis in solution: The study of various catalysed reactions in solution has also revealed that intermediate compounds are formed between the catalyst and the reactant. Some instances are cited here.

(*i*) Hydrobromic acid acts catalytically in the decomposition of hydrogen peroxide. It is most likely that the reaction proceeds through the intermediate formation of HBrO as:

$$\begin{array}{llcl} H_2O_2 & + H^+ + Br^- & \rightarrow & HBrO + H_2O \\ (HBrO & + H^+ + Br^- & \rightleftharpoons & H_2O + Br_2) \\ HBrO & + H_2O_2 & \rightleftharpoons & H^+ + Br^- + O_2 + H_2O \\ \hline & 2H_2O_2 & \rightarrow & 2H_2O + O_2 \end{array}$$

(*ii*) The reaction between ceric and thiosulphate ions is catalysed by iodide ions. The iodide ion is first acted by ceric ions producing iodine atom. The later is then transformed back by thiosulphate into iodide ion.

$$\begin{array}{lcll} (i)\ 2Ce^{++++} + 2I^- & \rightarrow & 2Ce^{+++} + I_2 & \text{(slow)} \\ (ii)\ I_2 + 2S_2O_3^{--} & \rightarrow & 2I^- + S_4O_6^{--} & \text{(rapid)} \\ \hline 2Ce^{++++} + 2S_2O_3^{--} & \rightarrow & 2Ce^{+++} + S_4O_6^{--} & \end{array}$$

The reaction rate depends upon the slow process (*i*) and hence on the concentration of the iodide ion.

(*iii*) $C_2H_5HSO_4$ is formed as an intermediate product in the preparation of ether from alcohol; H_2SO_4 is the catalyst.

$$C_2H_5OH + H_2SO_4 \rightarrow C_2H_5HSO_4 + H_2O$$

$$C_2H_5HSO_4 + HOC_2H_5 \rightarrow (C_2H_5)_2O + H_2SO_4$$

Acid-Base Catalysis: Among the homogeneously catalysed reactions, of special interest are the reactions catalysed by H^+, OH^- and other acids and bases (Brönsted). These reactions are of different types as illustrated by a few examples below:

(*i*) *Specific H^+-ion Catalysis:* Some reactions are catalysed by H^+-ion only: such as, the decomposition of formic acid, inversion of sucrose, decomposition of diazoacetic acid, etc.

(*a*) $HCOOH + H^+ \rightarrow (HCOOH_2)^+$; $(HCOOH_2)^+ \rightarrow CO + H_2O + H^+$

(*b*) $C_{12}H_{22}O_{11} + H_2O \xrightarrow{H^+} C_6H_{12}O_6 + C_6H_{12}O_6$

(*ii*) *Generalised acid catalysis:* There are reactions which are not only catalysed by H^+-ions but also by acids including water. The iodination of acetone into iodoacetone belongs to this category.

$$CH_3COCH_3 \rightarrow CH_3C(OH){=}CH_2 \xrightarrow{I_2} CH_3COCH_2I + HI$$

$$\text{The rate: } \frac{dx}{dt} = k_{H^+}.C_{H^+}.C_S + k_{H_2O}C_{H_2O}C_S + k_{HA}.C_{HA}C_S$$

C_S is the concentration of the substrate or reactant. The conversion of N-chloroacetanilide to p-chloroacetanilide belongs to this category.

(*c*) *Specific* OH^-*-ion catalysis:* The conversion of acetone into diacetone alcohol is catalysed only by OH^--ions.

$$2\,CH_3COCH_3 \xrightarrow{OH^-} CH_3COCH_2.C(CH_3)_2OH$$

$$\frac{dx}{dt} = k_{OH^-}\,C_{OH^-}\,C_S$$

(*d*) *Generalised base catalysis:* There are reactions like the decomposition of nitramide which are catalysed by OH^--ions as also by other bases (say. Ac^-).

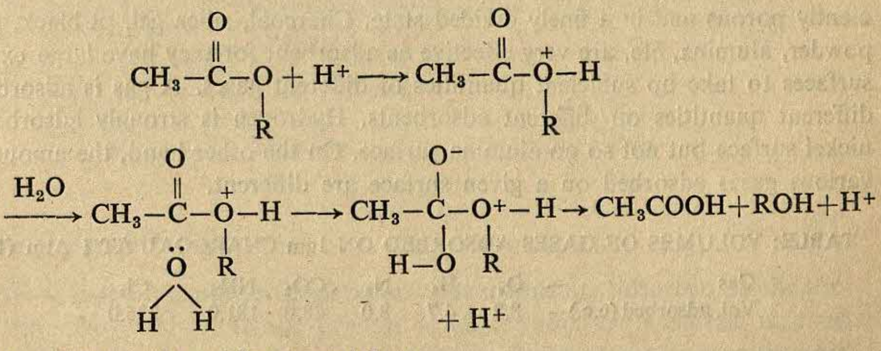
(*i*) $NH_2NO_2 + OH^- \rightarrow NHNO_2^- + H_2O$; $NHNO_2^- \rightarrow N_2O + OH^-$

(*ii*) $NH_2NO_2 + Ac^- = NHNO_2^- + HAc$; $NHNO_2^- \rightarrow N_2O + OH^-$

$HAc + OH^- \rightarrow Ac^- + H_2O$

(*e*) There are reactions which can be catalysed by both H^+ and OH^--ions. The hydrolysis of esters is the outstanding example.

(*a*) With H^+-ion as catalyst

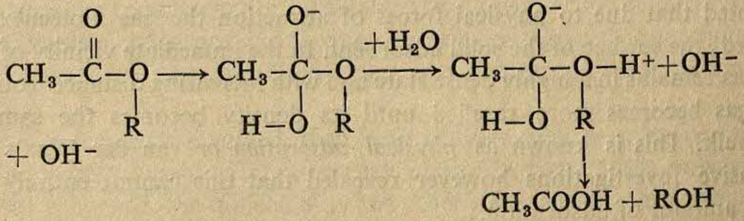


$$CH_3-\overset{\overset{O}{\|}}{C}-\underset{\underset{R}{|}}{O} + H^+ \longrightarrow CH_3-\overset{\overset{O}{\|}}{C}-\underset{\underset{R}{|}}{\overset{+}{O}}-H$$

$$\xrightarrow{H_2O} CH_3-\underset{\underset{\underset{H\quad H}{\ddot{O}}}{|}}{\overset{\overset{O}{\|}}{C}}-\underset{\underset{R}{|}}{\overset{+}{O}}-H \longrightarrow CH_3-\underset{\underset{H-O}{|}}{\overset{\overset{O^-}{|}}{C}}-\underset{\underset{R}{|}}{O^+}-H \rightarrow CH_3COOH+ROH+H^+$$

$$+\,H^+$$

(*b*) With hydroxyl ion as catalyst



$$CH_3-\overset{\overset{O}{\|}}{C}-\underset{\underset{R}{|}}{O} \longrightarrow CH_3-\underset{\underset{H-O}{|}}{\overset{\overset{O^-}{|}}{C}}-\underset{\underset{R}{|}}{O} \xrightarrow{+H_2O} CH_3-\underset{\underset{H-O}{|}}{\overset{\overset{O^-}{|}}{C}}-\underset{\underset{R}{|}}{O}-H^+ + OH^-$$

$$+\,OH^- \qquad\qquad \downarrow \qquad CH_3COOH + ROH$$

The rate of reaction is adequately expressed as

$$\frac{dx}{dt} = k_{H^+}C_{H^+}C_{ester} + k_{OH^-}C_{OH^-}C_{ester} + k_{H_2O}C_{H_2O}C_{ester}$$

The hetrogeneously catalysed reactions depend on the 'adsorption' of the reactants on solid surfaces. It would be useful to have some idea about adsorption before considering the heterogeneous catalysis.

18.4. Adsorption

When a component in a heterogeneous system penetrates into another and spreads throughout the bulk of the latter it is regarded as *absorption*, the first is absorbed by the second. Ammonia gas is absorbed by water when it comes in contact with it. But it is now well-known that often a component (A), instead of penetrating inside another, remains relatively more concentrated near or on the interface. The result is, the concentration of A in the vicinity of the interface is different from that in the bulk. This phenomenon is called **adsorption** and it is necessarily related to the surface.

If a finely divided solid (say, charcoal powder) is stirred into a dilute solution of methylene blue, the depth of colour of the solution decreases appreciably. Similarly, if a finely divided solid is added to a gas at low pressure, the gas pressure is found to decrease. In these instances, the dye or the gas concentrates on the surface of the solid and is said to have been adsorbed.

The substance on the surface of which adsorption occurs is the *adsorbent* and the substance adsorbed is termed *adsorbate*. The magnitude of adsorption depends upon (*i*) the nature of the adsorbent and its state of subdivision, (*ii*) the nature of the adsorbate and its concentration or pressure and (*iii*) the temperature.

For appreciable adsorption, the surface area of the adsorbent must be sufficiently porous and in a finely divided state. Charcoal, silica gel, pt-black, nickel powder, alumina, etc. are very effective as adsorbent for they have large exposed surfaces to take up sufficient quantities of different gases. A gas is adsorbed in different quantities on different adsorbents. Hydrogen is strongly adsorbed on nickel surface but not so on alumina surface. On the other hand, the amounts of various gases adsorbed on a given surface are different.

TABLE: VOLUMES OF GASES ADSORBED ON 1gm CHARCOAL AT 1 Atm (15°C)

Gas —	O_2	H_2	N_2	CO_2	NH_3	Cl_2
Vol. adsorbed (c.c.) —	8.2	4.7	8.0	48.0	181.0	235.0

Types of adsorption: For the mechanism of the process of adsorption, it is accepted that due to physical forces of attraction the gas molecules are drawn towards the surface of the solid adsorbent. In the immediate vicinity of the surface, the gas remains in a highly dense state and with increasing distance from the surface the gas becomes more rarefied until its density becomes the same as that in the bulk. This is known as *physical adsorption or* **van der Waals adsorption.** Intensive investigations however revealed that this cannot entirely explain the total amount of adsorption.

In 1916 Langmuir introduced a new concept involving chemical forces. According to him, in the interior of the solid adsorbent the atoms have their field of force wholly satisfied by the surrounding atoms. The atoms of the adsorbent on the surface are not completely surrounded and these have a residual force due to unshared electrons towards the exterior. This residual field leads to sharing of electrons with striking gas molecules and a sort of covalency-linking is formed between the adsorbate gas molecule and the surface atom. The distinction between this linkage and the formation of a chemical compound is that inspite of the electron sharing with the gas molecule, the surface-atom of the adsorbent remains simultaneously bonded with the other atoms in the crystal-lattice. The adsorption is thus chemical in nature and hence often called **chemisorption.**

It is further contended that (*i*) the surface of the adsorbent is a 'chequer-board' of atoms upon each of which a gas molecule may be adsorbed. (*ii*) The residual field of force extends approximately up to a distance equal to that of molecular diameter. Hence, once the surface atoms are covered up by the gas molecules, no further adherence of the gas molecules would occur, *i.e.*, the adsorbed gas is *unimolecular* in thickness. There is an equilibrium between the adsorbed molecules and the striking gas molecules. (*iii*) Since adsorption involves electron sharing, considerable heat-changes would occur resulting into activation of the adsorbed gas molecules. Fig (XVIII.2) represents Langmuir concept.

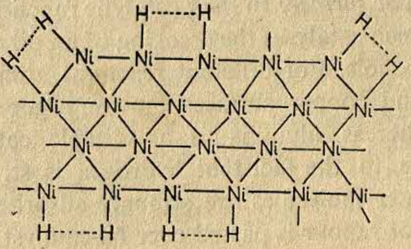


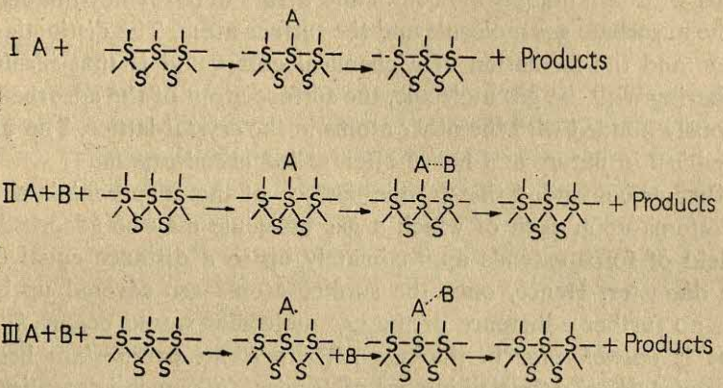
Fig. XVIII.2. Hydrogen chemisorbed on Nickel surface

18.5 Heterogeneous Catalysis

In heterogeneous catalysis the reactant or reactants are adsorbed on the surface of the solid catalyst. In the process of adsorption, the adsorbed reactant molecules are activated by the heat of adsorption. Being thus activated they are in a position to undergo transformation. If there be only one reactant to decompse, the molecules during adsorption not only become energy-rich but there is also a rearrangement in its atomic distribution (see decomposition of ethanol, fig. XVIII.4)

If there be two reactants involved, then both of them may be adsorbed and those in close proximity would react with each other. In some cases only one reactant would be adsorbed, the molecules of the other strike against the activated adsorbed molecule and the reaction occurs (See fig.XVIII.3). After reaction, the product molecules mostly fly off, leaving the surface free for fresh adsorption and reaction.

The solid catalyst has several functions: (*i*) it leads to adsorption and consequent activation, (*ii*) it stores the heat of reaction and provides the heat of activation, if need be (*iii*) it gives an opportunity to the adsorbed reactant molecules to redistribute its energy by weakening of its bonds as seen in adsorption of H_2 on nickel, fig. XVIII.2.



XVIII.3. Adsorption and reaction: S, solid molecules; A and B reactant molecules

Specificity of catalytic surface: In their catalytic functions, surfaces are specific in nature. A surface which catalyses the cracking of an oil may not at all influence the dehydration of alcohols. For different reactions, different catalytic surfaces are effective. Nickel and copper surfaces are very good catalysts for hydrogenation processes whereas alumina is a suitable catalyst for dehydration processes. This is due to the fact that hydrogen is strongly adsorbed on Ni or Cu-surface, and water molecules are strongly adsorbed on alumina surface. As a result when ethanol vapour is passed over Ni-catalyst it is oxidised to acetaldehyde but when it is passed over alumina, it is dehydrated to ethylene:

$$CH_3CH_2OH \xrightarrow{Ni} CH_3CHO + H_2 \parallel CH_3CH_2OH \xrightarrow{Al_2O_3} CH_2{=}CH_2 + H_2O$$

These are schematically represented in Fig. XVIII.4.

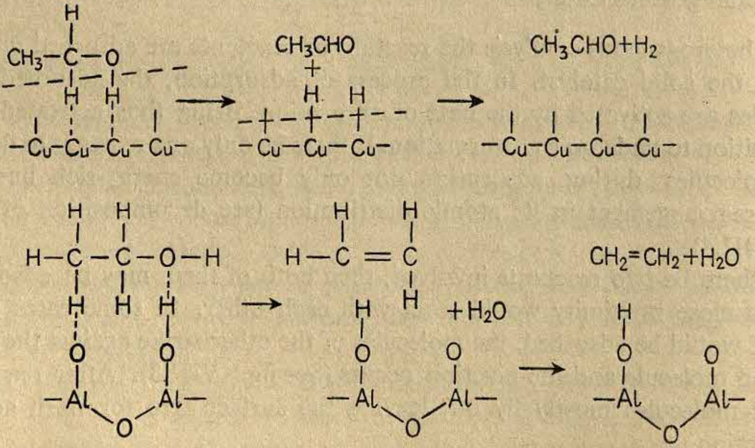


Fig.XVIII.4. Decomposition of ethanol on Ni and Al_2O_3 surfaces

This indicates that there is definite orientation of the adsorbate molecules on a given surface, which is responsible for different types of reaction. Some of the catalysts commonly used for different kinds of reaction are listed below:

Processes	*Catalysts*
(*i*) Hydrogenation/dehydrogenation	Ni, Cu, ZnO-Cr_2O_3
(*ii*) Dehydration/hydration	Al_2O_3
(*iii*) Cracking of petroleum fractions	SiO_2-Al_2O_3 gel
(*iv*) Synthesis of ammonia	Iron
(*v*) Polymerisation	$Al(Et)_3$, $TiCl_4$, phosphoric acid on keiselguhr

Another fact needs mention here. A solid surface, however smooth it may appear, has peaks, edges, corners, cracks, furrows,etc. at least on a scale of $5 \sim 10$Å. The residual field is not uniform on the surface. The adsorption is greater at the peaks or cracks where the field is stronger. It is agreed now that adsorption and subsequent reaction take place preferentially on certain parts of the surface called **active centres,** where the field is stonger.

Promoters: The activity of a catalyst is sometimes markedly enhanced by the addition of small amounts of a substance which has very little catalytic effect on the given reaction. This phenomenon is called *promoter action* and the added substance is *promoter*. The synthesis of NH_3 is catalysed by iron. But if a mixture of $K_2O + Al_2O_3$ is added to iron-catalyst its catalytic effect is much increased. The mixture $(K_2O + Al_2O_3)$ functions as promoter. The oxidation of iodide by persulphate, $S_2O_8^{--} + 2I^- \rightarrow I_2 + 2SO_4^{2-}$, is catalysed by Fe^{++} ions but very little by Cu^{++} ions. But if a mixture of Cu^{++} ions and Fe^{++} ions be used, the speed of the oxidation is very much enhanced. Cu^{++} ions act as promoter.

18.6. Negative Catalysis: Catalytic Poisons

In heterogeneous catalysis, it is often found that a small amount of a foreign substance added to the system impairs the catalytic activity considerably. These are called *Catalytic poisons.* These usually function in two ways: (*i*) The added substance may be preferentially adsorbed on the active centres preventing the reactant to be adsorbed and activated. Hence the rate of reaction is retarded. Thus, a small quantity of CO has a powerful retarding effect on the hydrogenation of ethylene on copper. (*ii*) The added substance may chemically interact with the catalyst producing thereby a new inert surface. The reaction rate is thus decreased. Thus, a trace of arsenic compound present in SO_2-gas practically stops the catalytic activity of platinum in contact process of H_2SO_4 manufacture. Arsenic forms an arsenide of platinum on the surface.

Inhibition in homogeneous catalysis also may be due to two reasons when foreign substances are added. (*i*) The added inhibitor may remove the catalyst present in the system by uniting with the latter. Thus, in the auto-oxidation of sulphite solutions catalysed by Cu^{++}, the rate of reaction will be much reduced on addition of KCN solution. This is due to the fact that the catalyst (Cu^{++}) is removed as cuprocyanide complex. (*ii*) On the other hand there are reactions which normally proceed in a chain mechanism. The function of the inhibitor is simply to break the chains thereby retarding the process. Benzaldehyde, glycerine, etc. function as inhibitor in this way during the oxidation of sulphite solutions in air.

The negative catalysts play a very important role in technology and industry, especially in the preservation of unstable substances. Thus (*i*) a little barbituric acid added to H_2O_2 prevents its decomposition, (*ii*) a trace of hydroquinone stabilises monomers. (*iii*) thiourea is used in prolonging the life of rubber, (*iv*) sodium benzoate is often added to food as preservative, (*v*) butoxy anisole is added to *vanaspati ghee* to prevent rancidity, (*vi*) lead tetraethyl is used as 'antiknock' in motor fuels, etc.

18.7 Enzyme Catalysis

Enzymes are complex protein substances produced by the living cells. They are responsible for catalysing infinite types of chemical changes occurring in living systems. Even when the enzymes are isolated from the cells, they retain their catalytic activity and function in the same fashion *in vitro*. The structure of a few enzymes, like insulin, has been recently established and a very few synthesised. The nobel-laureate Khorana has synthesised co-enzyme A, which plays an essential part in the oxidation processes in the living cells.

Enzymes are extremely specific in their catalytic functions. Thus, *catalase* obtained from plant cells will catalyse the decomposition of H_2O_2 only, *zymase* from yeast cells would ferment dextrose but will be ineffective in the breakdown of starch or canesugar, *urease* hydrolyses urea but not methyl urea, etc. Examples of a few enzymatic reactions are given below:

Enzyme	*Source*	*Catalytic function*
Amylase	pancreas	starch to maltose
Invertase	yeast	cane sugar to glucose and fructose
Zymase	yeast	glucose to alcohol
Urease	soya bean	urea to ammon. carbonate
Pepsin	gastric juice	proteins to peptones
Lipase	castor seed	sugar to glycerol
Ptylin	saliva	starches to sugar
Rennin	gastric juice	curdles milk

Every enzyme functions within a limited range of pH and within a limited range of temperature, beyond which they are almost ineffective. Most of the enzymes have an *optimum temperature*, when they would have maximum efficiency. The enzymes are often associated with some simpler molecules, called *co-enzymes*, during their catalytic activity. The enzymes are poisoned easily by CS_2, HCN, H_2S etc. The catalytic efficiency of enzymes is much greater than that of the inorganic catalysts. Also a minute amount of enzyme would catalyse the process of several million times the weight of the substrate.

Enzymatic Process : The mechanism of the enzymatic process is explained as follows: The enzyme (E) first forms a complex intermediate (ES) with the substrate

(S). The amount of the enzyme is quite small compared to the amount of the substrate. The intermediate complex then decomposes into the product reproducing the enzyme.

$$E + S \underset{k_2}{\overset{k_1}{\rightleftharpoons}} (ES) \xrightarrow{k_3} E + P \text{ (products)}$$

When the reaction proceeds smoothly under steady state conditions, the rate of change of conc. of the complex (ES] is zero, *i.e.*

$$\frac{d[\mathrm{ES}]}{dt} = 0.$$ The square brackets indicate concentration.

$$\text{Now } \frac{d[\mathrm{ES}]}{dt} = k_1[\mathrm{E}][\mathrm{S}] - k_2[\mathrm{ES}] - k_3[\mathrm{ES}] = 0$$

If $[\mathrm{E}]_0$ is the total molar conc. of the enzyme and the rate is measured when the substrate conc. has not changed much,

$$[\mathrm{E}]_0 = [\mathrm{E}] + [\mathrm{ES}]$$

$$\therefore \quad k_1([\mathrm{E}]_0 - [\mathrm{ES}])[\mathrm{S}] - (k_2 + k_3)[\mathrm{ES}] = 0$$

$$\therefore \quad [\mathrm{ES}] = \frac{k_1[\mathrm{E}]_0[\mathrm{S}]}{k_1[\mathrm{S}] + (k_2 + k_3)} = \frac{[\mathrm{E}]_0}{1 + \frac{(k_2 + k_3)}{k_1[\mathrm{S}]}}$$

$$= \frac{[\mathrm{E}]_0}{1 + \frac{k_m}{[\mathrm{S}]}}$$

where $(k_2 + k_3)/k_1 = k_m$, called *Michaelis constant.*
Now rate of formation of the product (P) is given by

$$\frac{d[\mathrm{P}]}{dt} = k_3[\mathrm{ES}] = \frac{k_3[\mathrm{E}]_0}{1 + k_m/[\mathrm{S}]}$$

When [S], the substrate concentration, is very large then with a given concentration [E] of enzymes,

$$\text{Rate} = \frac{d[\mathrm{P}]}{dt} = k[\mathrm{E}] = \text{constant}$$

Hence, with large concentration of the substrate, enzymatic process would be of the *Zero order*.

The enzymes play the most vital role in the metabolic processes in the living systems. They are responsible for the transformation of food into structural molecules for growth. Besides, many an industry such as the manufacture of sugar, glucose, alcohol, acetic acid, curd, cheese, etc. are based primarily on different enzymatic actions.

18.8. Autocatalytic Reactions

Sometimes one of the products of a reaction is capable of accelerating the rate of the reaction. Such a reaction is called an *autocatalytic* reaction. Thus, in the hydrolysis of esters, the acid produced in the reaction also catalyses the reaction. In the hydrolysis of ethyl acetate catalysed by acetic acid, let the initial concentration of ester be a and of acetic acid be b; suppose x is the amount of ester hydrolysed at time t, then

$$\frac{dx}{dt} = kb(a-x) + kx(a-x) = k(a-x)(b+x)$$

On integration and remembering when $t=0$, $x=0$, we have

$$k = \frac{1}{t(a+b)} ln \frac{a(b+x)}{b(a-x)}.$$

Other common examples of autocatalysis is found in the oxidation of oxalic acid by $KMnO_4$ soln in which the product Mn^{++} ions act as catalyst, the reaction becoming faster and faster with time. Again, the dissolution of copper by nitric acid is initially slow but as nitrous acid is produced the rate is much enhanced, for, the latter is a strong catalyst for the process.

18.9. Induced Reactions: Sodium sulphite solution is spontaneously oxidised in air, but sodium arsenite solution exposed to air is not oxidised· But if a mixture of the solutions of sodium sulphite and sodium arsenite are kept in air, both of them are found to be oxidised. Such cases are called '*Induced Reactions*', sodium arsenite is oxidised by induction. It is found that sodium arsenite is really involved in breaking the chains of sodium sulphite oxidation and in this act it combines with chain carriers leading to its own oxidation.

18.10. The importance of enzymatic catalysis in industry and technology has already been mentioned. Many other industries are entirely dependent on catalysis. Only a few of them are listed below:

CATALYSED INDUSTRIAL PROCESSES

Industrial Process	*Catalysed by*
1. Contact Process for H_2SO_4	Pt, V_2O_5
2. Haber's synthesis of ammonia	Fe
3. Ostwald Process for HNO_3 manufacture	Pt-gauze
4. Hydrogenation of oils	Ni
5. Methyl alcohol from H_2 and CO	$ZnO + Cr_2O_3$
6. Hydrocarbons from H_2 and CO (Fischer–Tropsch)	Co, ThO_2
7. Synthetic petrol from coal (Bergius)	Iron oxalate
8. Acetaldehyde from acetylene	$HgSO_4$
9. Phthalic acid from naphthalene	$HgSO_4$
10. Cracking of petroleum fractions	Silica gel
11. Styrene to polystyrene	Peroxides
12. Alkylation of benzene	$AlCl_3$

EXERCISES

1. Explain and illustrate (*i*) catalysis and (*ii*) catalysts.

Differentiate, with examples, between homogeneous and heterogeneous catalysis. (Kurukshetra, 1974)

Where are the following catalysts used: iron, Pt-gauze, nickel, $HgSO_4$ and zymase?

2. Explain the phenomenon of catalysis. Describe some applications of catalysis in the laboratory and in industry. (*Gauhati* '73).

3. Discuss the various theories of catalysis. (*Udaipur* 1970, *Lucknow* '71, *Bangalore* '74)

4. Write explanatory notes on (*i*) Promoters (*ii*) negative catalysts (*iii*) catalytic poisons (*iv*) specificity in the action of catalysts.

5. What are meant by (*i*) auto-catalysis (*ii*) induced reactions (*iii*) enzymes?

6. Give the essential features of catalytic reactions. Can a catalyst increase the yield of a reaction? (*Calicut* '72)

7. Give an account of the action of enzymes as catalysts choosing your examples of everyday interest. (*Delhi* '71, *Lucknow* '71, *Bangalore* '73)

8. Write notes on:

(*a*) Theory of heterogeneous catalysis (*Delhi Univ.* '70)

(*b*) Mechanism of catalytic reactions (*Delhi Univ.* '72)

(*c*) Characteristics of a catalyst (*Punjabi Univ.* '71)

9. How does the concept of activation energy explain the role of catalysts? How does a catalyst affect a reversible reaction in eqm? Give reasons for your answer. (Kurukshetra Univ. '73)

10. Discuss the statement that the general function of a catalyst is simply to provide an additional mechanism by which reactants can be converted into products. (Kerala Univ. '72)

CHAPTER 19

PHOTOCHEMISTRY

19.1 Photochemical Reactions

The reactions, ordinarily carried out in the laboratory and for which the kinetics and mechanism have been so far discussed, are called 'thermal' or dark reactions. Many substances, on exposure to electromagnetic radiations, such as X-rays, γ-rays, visible and ultraviolet rays, undergo chemical changes. When chemical changes occur in consequence of absorption of photons from the visible and ultraviolet radiations having wavelengths approximately between 10000Å and 1000Å, the reactions are called **photochemical reactions.** The energy in this range varies from 30000 cal to 286000 cal per mole. Photochemistry concerns itself with the reactions effected with visible and ultraviolet radiations. On the other hand, X-ray or γ-ray photons or high energy particles such as α-rays, β-rays, neutrons etc. cause drastic changes, on molecules coming in their path. The study of the effect of these radiations comes in the field of 'Radiation chemistry'.

A word on the difference of photochemical and thermal reactions may be noted. The thermal reactions are profoundly affected by temperature and have large temperature coefficients. But photochemical reactions are practically independent of temperature. A thermal reaction is always associated with a decrease in free energy, but there are some photochemical reactions with increase in free energy as in 'photosynthesis'.

19.2 Absorption of light

The amount of light absorbed is obtained by measuring the intensity of the incident and emerging radiation of a given wavelength. The decrease in intensity of the radiation during its transmission through the absorbing medium is governed by two laws.

(*i*) **Lambert's Law:** This law states that in the case of a pure liquid *the rate of decrease of intensity with the thickness of the absorbing medium is proportional to the intensity of the penetrating radiation.* Consider a thin layer of the medium of thickness dl and the intensity of radiation entering be I then,

$$\frac{dI}{dl} = -kI, \quad \text{or,} \quad \int_{I_0}^{I} \frac{dI}{I} = -\int_{0}^{l} k\,dl$$

i.e. $$ln\ (I/I_0) = -kl, \quad \text{or,} \quad I = I_0 e^{-kl} \qquad \text{...(XIX.1)}$$

where I_0 is the intensity at incidence and I at distance l.

Rewriting XIX.1, $$I = I_0 10^{-\alpha l} \qquad \text{...(XIX.2)}$$

where $\alpha = 0.4343k$, a constant, called '*extinction coefficient*'.

Hence $\frac{I_0-I}{I_0} = [1-10^{-al}]$, which shows that the fraction of radiation absorbed, will be the same for equal thickness independent of the incident intensity.

(*ii*) **Beer's Law:** When the absorbing substance is present in solution, the absorption of light depends also upon the concentration. Beer's Law states that *the rate of decrease of intensity of radiation observed with the thickness of the medium is proportional to intensity of the radiation and the concentration of the solute.* As before, using the same symbols, we have for concentration, C,

$$\frac{dI}{dl} = -k'CI, \quad \text{or,} \quad I = I_0 e^{-k'cl}$$

Rewriting $\quad I = I_0\, 10^{-0.4343k'cl} = I_0 10^{-\epsilon cl}$ . . . (XIX.3).
where ϵ is called the *molar extinction coefficient.*

Problem: 2.5 mm thickness of a liquid transmitted 60% of the incident light. What percentage will be transmitted by 0.5 mm thickness of the same liquid?

$I/I_0 = 0.6$; let the required percentage be x.

From eqn. (XIX.2), $\ln \frac{I}{I_0} = -al.$

$$\therefore \quad \ln x = -a \times 0.5$$

$$\ln 0.6 = -a \times 2.5$$

or $\quad \frac{\ln x}{\ln 0.6} = \frac{1}{5}$ or $\log x = \frac{1}{5}\log 0.6$, when $x = 90.28\%$

19.3. The Laws of Photochemistry

The photochemical reactions, are governed by two basic principles, the Grotthuss-Draper Law and the Einstein Law of photochemical equivalence.

1. The **Grotthuss-Draper Law** *states that only those radiations which are absorbed can be effective in producing the chemical change.* The photochemical reaction is the result of absorption of light but absorption of light may not always lead to chemical reaction. Sometimes the absorption of photon may only increase the thermal energy or the absorbed radiation may be re-emitted.

2. **The Einstein Law of Photochemical Equivalence** states that *each molecule taking part in a chemical reaction, which is a direct result of the absorption of light, takes up only one quantum of radiation causing the change.* If the reaction takes place in several steps then 'each quantum of radiation absorbed by a molecule activates one molecule in the primary step of a photochemical process'.

In the initial step or primary process, a molecule is activated by absorption of one quantum of radiation. If it reacts immediately then the number of molecules transformed would be equal to the number of quanta absorbed. But if some activated molecules are deactivated by collision before undergoing chemical change, then the number of molecules transformed would be less than the number of quanta absorbed. Or, if the reaction involves chain mechanism then a large number of molecules would react from one quantum absorbed in the primary step.

The efficiency of a photochemical process is expressed in terms of *quantum yield* (ϕ) which is defined as the number of molecules reacting per quantum of light absorbed.

$$\text{Quantum yield, } \phi = \frac{\text{no. of molecules reacting}}{\text{no. of quanta of radiation absorbed}}$$

If the light absorbed has a frequency ν per sec or wavelength λ in cm, then its energy is $h\nu$ ergs. The energy absorbed per mole, according to the law of photochemical equivalence, is

$$E = N_0 h\nu = \frac{N_0 hc}{\lambda} \text{ ergs per mole}$$

Since $c = 2.998 \times 10^{10}$ cm/sec, $h = 6.625 \times 10^{-27}$ ergs-sec and $N_0 = 6.02 \times 10^{23}$

we have, $$E = \frac{1.196 \times 10^8}{\lambda} \text{ ergs per mole} \qquad \ldots \text{(XIX.4)}$$

If λ be expressed in Angström units, ($1\text{Å} = 10^{-8}$ cm),

$$E = \frac{1.196 \times 10^{16}}{\lambda} \text{ ergs per mole} \qquad \ldots \text{(XIX.5)}$$

or, $$E = \frac{2.859 \times 10^5}{\lambda} \text{ kilocalories per mole} \qquad \ldots \text{(XIX.6)}$$

This energy (E) which activates one mole of the reactant *i.e.*, the energy corresponding to Avogadro number of photons is called **one einstein.** It is evident the energy will be greater lower the wavelength. So an einstein corresponding to violet or ultraviolet radiations would involve more energy than one in the visible red region.

TABLE: ENERGY OF DIFFERENT RADIATIONS

Wave length λ (Å)	*Frequency* ν	*Description*	*Energy*
			calories/mole
10^5	3×10^{13}	Infra red	2860
10^4	3×10^{14}	Near infra red	28600
8000	3.75×10^{14}	Red	35700
5000	6×10^{14}	Blue	56900
4000	7.5×10^{14}	Violet	71500
1000	3×10^{15}	Ultra violet	286000
1	3×10^{18}	X-rays	2.86×10^8
0.01	3×10^{20}	γ-rays	2.86×10^{10}

Problem: In the photochemical combination of H_2 and Cl_2 a quantum efficiency of 1×10^6 is obtained with a wavelength of 4800 Å. How many moles of HCl would be produced under these conditions per calorie of radiation energy absorbed (Calicut Univ.'72).

$$\text{Energy per quantum, } \epsilon = \frac{hc}{\lambda} = \frac{6.62\times10^{-27}\times3\times10^{10}}{4800\times10^{-8}\times(4.2\times10^{7})}\text{ cal}$$

no. of quanta per calorie of this radiation,

$$x = \frac{1}{\epsilon} = \frac{48\times4.2\times10}{6.62\times3\times10^{-17}} = 1.01\times10^{19}$$

$\therefore$ no. of molecules reacting $= 1.01\times10^{19}\times1\times10^{6} = 1.01\times10^{25}$

$\therefore$ no. of moles reacting $= 1.01\times10^{25}/6.02\times10^{23} = 16.8$ moles.

No. of moles of HCl produced $= 2\times16.8 = 33.6$ moles

Experimental arrangement. A schematic representation of the experimental arrangement required in studying photochemical reactions is given in Fig. XIX.1. The reactants are taken in a glass or quartz cell X whose walls are optically plane. The cell is kept in a constant temperature bath D. From the light source (L) the radiations are passed through a condenser system (A) when a parallel beam is formed. Different gas-discharge tubes, metal-arcs, filament-lamps are used as light source (L) depending upon the required spectral range. The parallel beam then passes through a filter or monochromator B, so that a beam of only definite wavelength may come out to enter the reaction vessel (X) after its passage through the slit C and window (W_1).

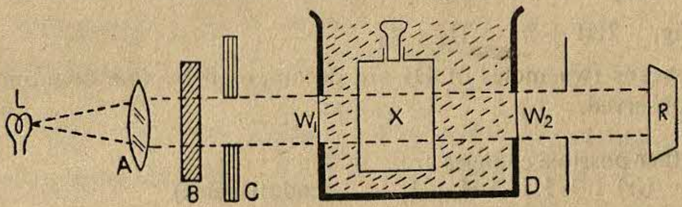


Fig. XIX.1. Experimental arrangement for studying photochemical reactions (schematic)

After absorption in the reaction vessel, the residual portion of the radiations passes through the window (W_2) and finally enters a photocell or thermopile, etc. in which the intensity of the radiation could be measured. When ultraviolet radiations are used, all transparent parts are made of quartz.

The thermopiles are multithermocouple junctions, previously calibrated against standard light sources. So, when the unabsorbed radiations fall on them, the intensity of the same is known. Sometimes chemical actinometers are employed. These contain reactants sensitive to light. A commonly used actinometer is the uranyl oxalate actinometer (see Sec. 19.5.).

19.4. Photochemical Reactions

The photochemical reactions belong to two categories. (*i*) In some cases the absorption of radiation activates the reactant leading directly to the chemical change. In such cases the quantum yield is unity.

Example: $CH_2ClCOOH + H_2O + h\nu \rightarrow CH_2OHCOOH + HCl$

Of course, very few reactions of this type are known. The reaction, $2Fe^{++} + I_2 + h\nu \rightarrow 2Fe^{+++} + 2I^-$, has also quantum yield of unity.

II. In most of the photochemical reactions, in the *primary process*, the radiations are absorbed activating a molecule to energy-rich state or to its dissociation. Different types of *secondary processess* then follow which are thermal changes. Some typical examples are given here.

Typical Photochemical processes: (1) *Decomposition of HI.* In the gas phase, HI absorbs radiation in the wave-length region 2100 ~ 2820 Å. It has been observed that the quantum yield in photochemical decomposition of HI is 2 moles/einstein. In the *primary process*, one quantum of radiation is absorbed by a molecule of HI, resulting into its dissociation into atoms.

(*i*) $HI + h\nu \rightarrow H + I$

This is followed by thermal processes (*ii*) & (*iii*),

(*ii*) $H + HI \rightarrow H_2 + I$

(*iii*) $I + I \rightarrow I_2$

Adding, $2HI + h\nu \rightarrow H_2 + I_2$

This means two moles of HI are decomposed by one quantum, as experimentally observed.

The other possible changes are

(*iv*) $I + HI \rightarrow H + I_2$ (endothermic)

$$\left.\begin{array}{l}(v)\ I + H \rightarrow HI \\ (vi)\ H + H \rightarrow H_2\end{array}\right\}\ \text{(exothermic)}$$

The process (IV) being endothermic seldom occurs at ordinary temperature while processes (*v*) and (*vi*) are highly exothermic and the products immediately break up. The process $I + H_2 \rightarrow HI + H$ is too slow due to high energy of activation and would scarcely occur. Hence there is no possibility of a chain reaction.

(2) *Photochemical combination of H_2 and Cl_2*: The quantum yield in this reaction is very large and of the order of 10^6. The primary process is the absorption of a quantum of radiation (wave length, ~4800Å) by a chlorine molecule, which dissociates into atoms.

(*i*) $Cl_2 + h\nu \rightarrow Cl + Cl$

This is followed by secondary processes,

(*ii*) $Cl + H_2 \rightarrow HCl + H$

(*iii*) $H + Cl_2 \rightarrow HCl + Cl$

The processes (*ii*) and (*iii*) produce HCl and also the atomic H and Cl. The latter cause repetition of processes (*ii*) and (*iii*) a large number of times leading to a chain reaction. That is why the quantum yield is very large (10^6). The Cl and H atoms are the chain carriers. The chain is terminated by a chance reaction; $Cl + Cl \rightarrow Cl_2$.

(3) *Decomposition of nitrosyl chloride:* In the examples cited above absorption of radiation produces atoms, which take part in subsequent secondary processes. The absorbed quantum may energise the reactant molecule sufficiently to undergo

the change. The absorbed radiation may also produce radicals for the secondary processes. For example, the photochemical decomposition of nitrosyl chloride follows the mechanism:

$$NOCl + h\nu \rightarrow (NOCl)^*$$
$$(NOCl)^* + NOCl \rightarrow 2NO + Cl_2$$

That is, two moles of NOCl would decompose per einstein. In fact, at ~ 6300Å, the quantum yield is two.

(4) *Photochemical Decomposition of acetaldehyde:* Acetaldehyde absorbs radiation at < 3000Å and breaks up into radicals in the primary process. The radicals lead to a chain reaction, as;

(*i*) $CH_3CHO + h\nu \rightarrow CH_3 + CH_3CO$

(*ii*) $CH_3 + CH_3CHO \rightarrow CH_4 + CH_3CO$

(*iii*) $CH_3CO \rightarrow CH_3 + CO$

(*iv*) $2CH_3 \rightarrow C_2H_6$

The kinetics of this mechanism gives, $\frac{d}{dt} C_{CH_4} = kI^{\frac{1}{2}} C_{acetaldehyde}$ which has been experimentally established.

19.5. Photosensitized Reaction

Photosensitized reactions constitute a separate group of photochemical reactions. In these reactions, the reactants are insensitive to the light to which they are exposed and as such these reactants do not take part in the primary step of absorption of radiation and dissociation. However when a suitable foreign matter is mixed with the reactants, the former will absorb the radiation and become excited. Subsequently, the excited foreign matter will pass on the energy to the reactant molecules which will undergo dissociation or chemical transformation. Processes of this nature are termed *photosensitized reactions* and the foreign substance which absorbs and transfers the energy of radiation is called the *photosensitizer*. Mercury or cadmium vapours are often used as sensitizers.

To illustrate, (*i*) when a mixture of H_2 and O_2 is exposed to radiations from a mercury lamp, $\lambda = 2537$Å, there is no change observed. Now if a small amount of Hg-vapour be mixed with the reactants, the Hg-atoms take up the radiation and become excited atoms. The excited mercury then transfers the energy (112000 cal/mole) by collision to hydrogen dissociating it. In this dissociation about 103000 cal are used up, the residual amount of energy is utilised in increasing translational energy. By transfering this energy, the excited mercury atom is said to be *quenched*.

$$Hg + h\nu = Hg^*$$
$$Hg^* + H_2 = 2H + Hg$$

The atomic hydrogen so produced will then carry on with the usual chain reactions to produce water.

Amongst many other mercury-photosensitized reactions, we may mention decomposition of ammonia, arsine, various alcohols, acids, etc; hydrogenation of ethylene, carbon monoxide, etc. Chlorine is a good sensitizer for synthesis of H_2O, decoposition of O_3 and for the reaction $2CO + O_2 \rightarrow 2CO_2$ ($\lambda \sim 4300$Å).

(*ii*) The photochemical decomposition of oxalic acid is sensitized by uranyl ion UO_2^{++}. This is employed in *chemical actinometers*. The uranyl oxalate actinometer contains a mixture of 0.04M oxalic acid and 0.01M uranyl sulphate. On exposure to radiation, the change occurring is

$$H_2C_2O_4 \rightarrow CO + CO_2 + H_2O$$

The energy absorbed by UO_2^{++} is transferred to the oxalic acid. The amount of reaction is measured by titrating back the residual oxalic acid with $KMnO_4$ solution. The uranyl ion does not change. In the range 2540$\sim$4350Å, each mole of oxalic acid decomposed is equivalent to 1.75 einsteins. The intensity in the experiment concerned is evaluated from this standard value.

(*iii*) The most outstanding example of photosensitization is the photosynthesis of carbohydrates in plants, in which the green colouring matter chlorophyll is the photosensitizer. Chlorophyll absorbs visible light in the region 6000–7000Å and this absorbed energy is then passed on to the reactants ($CO_2 + H_2O$) to form the basic molecule of the carbohydrate as

$$xCO_2 + xH_2O + zh\nu \rightarrow (CH_2O)_x + xO_2$$

The exact process is a very complicated one. Several quanta are required for each molecule of CO_2 and H_2O taking part.

(*iv*) *Photography:* The photographic films are coated with an emulsion of gelatine–silver bromide, which is sensitive to blue and violet radiations of the visible light. It is unaffected by lower-energy visible radiations such as green or red. On exposure, a AgBr molecule absorbs a quantum of light.

$$AgBr + h\nu \rightarrow Ag + Br$$

The exposed plate is then developed by immersing in a solution of light reducing agent like pyrogallic acid. The exposed parts are readily reduced to metallic silver, the amount of reduction is proportional to the intensity of light on a particular portion. This change is called 'developing'.

After developing, the unexposed parts are dissolved out by treatment with sodium thiosulphate solution, called 'fixing'. This is how the 'negative' is obtained, bright parts of the object becoming dark spots in the negative.

Now-a-days *orthochromatic* and *panchromatic* films for colour-photography are made on the principle of photosensitization. A film with aniline dye mixed with the emulsion is sensitive to green light. Films dyed with eosin are sensitive to green, yellow and orange radiations of the spectrum. These are *orthochromatic* films. Addition of dicyanin, erythrosin, etc. sensitizes the films even to the red portion of the spectrum and the latter are called *panchromatic* films. These films are now in extensive use.

19.6. Photochemical Equilibrium

The chemical equilibrium of a thermal reversible process is greatly influenced if light is absorbed either in the forward or the backward process. Thus the absorption of light by the reactant in the forward process will increase the speed of the forward reaction, but will not influence the rate of reverse thermal reaction. Due to increased concentration of the products, the rate of the reverse thermal process may increase to some extent. Ultimately however a balance between the rates of forward and backward reactions will be reached, in which the concentration of the products will be different from that in the thermal equilibrium. This balanced state is not really the true equilibrium state of the system but is existent in presence of light. This is a stationary state, often called a *photostationary* equilibrium. The best example, to illustrate this phenomenon, is the dimerization of anthracene. If 'A' denotes an anthracene molecule, the reaction is

$$2A \rightleftharpoons A_2$$

But the dimerization of anthracene in benzene solution can be carried out photochemically with ultraviolet light. The opposite change, the conversion of dimers into monomers is a thermal process.

$$2A \underset{\text{thermal}}{\overset{\text{light}}{\rightleftharpoons}} A_2$$

The anthracene in solution on being irradiated with ultraviolet light absorbs a quantum and becomes excited. The excited molecule (A^*) forms a dimer by collision with a normal molecule. The different steps in the system are

(1) $A + h\nu \rightarrow A^*$ (excitation) (3) $A_2 \rightarrow 2A$ (thermal)

(2) $A^* + A \rightarrow A_2$ (dimerisation)

Other instances of photostationary equilibria are the decomposition of O_3, NO_2, etc.

Instances of photostationary state are also known where both the forward and the backward processes are photosensitive, as in the case of

$$2SO_3 \underset{h\nu'}{\overset{h\nu}{\rightleftharpoons}} 2SO_2 + O_2$$

The photochemical efficiency in the two directions are not the same and the eqm. constant also differs from that for the pure thermal process.

19.7. Flourescence and Phosphorescence

It is commonly noticed that if a metal is heated to high temperature, it first becomes 'red hot' and then 'white hot'. That is, the body is made to emit visible radiations through the application of heat. However, if such emission of radiations occurs from a body due to the application of agency other than heat, the emitted radiation is called *Luminescence*. Luminescence may be of different types such as fluorescence, phosphorescence, etc.

1. **Resonance radiation.** When an atom or molecule absorbs light, it is excited to a higher electronic level. If the absorbed energy is almost immediately emitted back within a time interval of about 10^{-8} seconds and the emitted radiation has the same frequency, it is called 'resonance radiation'. Such cases often are found with atoms absorbing light waves. $A + h\nu \rightarrow A^*$; $A^* \rightarrow A + h\nu$

2. **Fluorescence.** But if the emitted radiation has a frequency less than that of the absorbed radiation it is called 'fluorescence'. The absorbed energy shall be released within 10^{-8} seconds but it may come out in successive stages.

$$A + h\nu \rightarrow A^* \qquad \begin{aligned} A^* &\rightarrow A' + h\nu' \\ A' &\rightarrow A + h\nu'' \end{aligned}$$

i.e., radiations of different frequencies may be emitted. The emission in fluorescence shall cease as soon as the light source is removed. Various fluorescent substances are well-known. The minerals fluorite, petroleum; the organic dyes like eosin, fluorescein; compounds like chlorophyll, ultramarine, riboflavin, etc. exhibit fluorescence either with visible light or ultraviolet irradiation.

3. **Phosphorescence.** Certain molecules after being excited by absorption of visible or ultraviolet radiation emit the radiations slowly and even long after the light source is removed. This is known as 'phosphorescence'. Zinc sulphide, alkaline earth sulphides are good examples of such phosphorescent substances.

4. **Chemiluminescence.** If at ordinary temperatures, light is emitted as a result of chemical reactions, the phenomenon is termed chemiluminescence. At ordinary temperatures, emission of light is not expected from substances. The emission occurs at the expense of some amount of heat of reaction. A portion of the heat of reaction activates some molecules of the system and the excited molecules then emit the energy as radiation. The glow of yellow phosphorus in air at room temperature producing 'cold light' is a common laboratory experience. During the auto-oxidation of some Grignard reagents, or alkaline solution of 5-aminophthalic hydrazide, etc. such chemiluminescence is observed. The glow of fireflies is due to the chemiluminescence of a protein (luciferin) oxidation by oxygen in presence of an enzyme. The decay of wood and vegetation over marshy places is often accompanied with chemiluminescence.

EXERCISES

1. (*a*) State Beer's Law and explain what is meant by molar extinction coefficient.
(*b*) What is meant by 'quantum yield'?

2. A compound absorbs ultraviolet radiation of wavelength 3000Å. What will be the total energy in kcal absorbed by one mole of the compound when irradiated with this radiation? (C.U. '74)

3. State Einstein Law of photochemical equivalence and discuss the relation,
(*i*) where the law is followed
(*ii*) where deviations take place (*Gauhati* '73)

4. State and explain the Law of photochemical equivalence. How are the discrepencies between the experimental results and this law explained? (*Panjabi* '72, *Udaipur* '74)

5. Explain with illustration, what is meant by photochemical equilibrium.

6. Write notes on:
(*i*) photosensitization (*ii*) chemiluminescence (Lucknow '73)

7. State Einstein Law of photochemical equivalence.
The quantum yield in the combination of H_2 and Cl_2 is 10^5 whereas it is only 0.5 when hydrogen combines with iodine. Why?

8. Write explanatory notes on (*i*) Fluorescence (*ii*) Phosphorescence.

9. If 2 mm thick plate of a material transmits 70% of the incident light, what percentage will be transmitted by 0.05 mm thick plate? (Andhra Univ. '75)

10. Calculate the energy in calories per mole for ultraviolet light of wavelength 2000Å.
[Ans. 142.95 kcal]

11. How many ergs of radiation of wavelength 250 $\mu\mu$ are required to decompose 0.001 mole A in the reaction $A \rightarrow 2B$, if $\phi = 2$ molecules per quantum. (North Bengal Univ. '67).

12. The photochemical decomposition of HI vapour was carried out with $\lambda = 2070$Å. Absorption of each calorie gave 1.44×10^{-5} gm H_2. What is the quantum yield? (Jad. Univ. '73)
[Ans. 2]

CHAPTER 20

ELECTROCHEMISTRY I
IONISATION & CONDUCTANCE OF SOLUTIONS

20.1. Electrolytes

Substances like glass, wax, mica, wood, kerosine, etc. strongly resist the flow of electricity through them and are called *non-conductors*. There are other substances such as the metals (Ag, Cu, Zn, Al, Fe, etc.), aqueous solutions of acids, bases, salts through which electric current can easily pass are called *conductors*. The conductors are divided into two classes:

(*i*) *Electronic or metallic conductors*, such as, Pt, graphite, Zn, Cu, etc. where there is no change of the conductor due to the passage of electricity. The electricity is carried by the transport of electrons.

(*ii*) *Electrolytic conductors or electrolytes*, such as the fused salts, bases, acids, etc. or more commonly the aqueous solutions of salts, acids, bases. The passage of electricity through these leads to decomposition of these substances. The electricity here is carried by transport of matter.

Substances which conduct electricity and simultaneously undergo chemical decomposition are *electrolytes*. The decomposition of the electrolyte due to the passage of electricity is called *electrolysis*. Electrolytes conduct electricity only in a molten state or in a state of solution but cannot do so in the solid state. The current enters or leaves the electrolyte through some rods or strips of metals or graphite, etc. partially immersed in the electrolyte; these are called *electrodes*. The electrode which is connected to the positive terminal of the battery is the positive electrode called ANODE and the electrode connected to the negative terminal of the battery is the negative electrode called CATHODE. The current is supposed to enter the electrolyte through the anode and leave it through the cathode. The apparatus in which electrolysis is carried out is called a *voltameter*. It is easy to conceive that the anode or the positive electrode has a deficiency of electrons and would readily accept electrons, whereas the cathode or the negative electrode has an abundance of electrons and would easily give away electrons. Though the current flows through the bulk of the electrolyte but electrolysis occurs only on the electrodes. Long before anything was known about the mechanism of transport of electricity through the electrolyte, Faraday made extensive study of electrolysis and found that there is a quantitative relation between the quantity of electricity flowing and the amount of chemical change occurring at the electrodes. The quantitative relations discovered by him are known as 'Faraday's laws'.

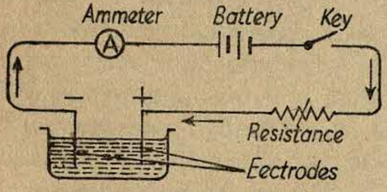


Fig. XX.1. Voltameter

20.2. Faraday's Laws of Electrolysis

The two laws established by Faraday (1833) are stated as follows:

(*i*) **The First Law.** *The amount of chemical change occurring at any electrode is strictly proportional to the quantity of electricity passed through the electrolyte.*

If W gm of a substance is deposited (or dissolved) at an electrode on passing Q coulombs of electricity, then

$$W \propto Q, \qquad \text{or} \quad W = zQ = zIt \qquad \ldots (\text{XX}.1)$$

where z is a constant called the electrochemical equivalent of the substance deposited. I amperes of current have passed for t seconds, so that, $Q = It$.

When 1 coulomb of electricity is passed ($Q = 1$), then $W = z$. This means that *the electrochemical equivalent is the quantity of substance formed at an electrode when one coulomb of electricity is passed.*

It has been found that on passing 1 coulomb of electricity 0.0000104 gm hydrogen, 0.001118 gm silver, 0.0003294 gm copper, etc. are deposited at the electrodes when suitable electrolytes such as, dil H_2SO_4, $AgNO_3$ solution, $CuSO_4$ solution are electrolysed. Hence these quantities are the 'electrochemical equivalents' of those elements.

(*ii*) **The Second Law:** *When different compounds are decomposed by the same quantity of electricity, the amounts of products obtained at different electrodes are proportional to their chemical equivalents.*

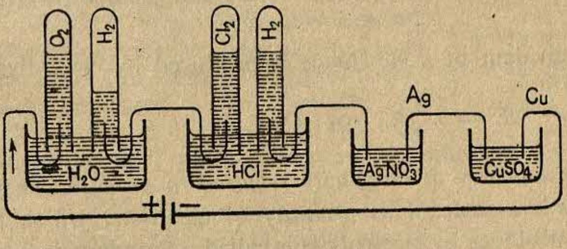


Fig. XX.2. Electrolysis of different substances

Suppose W_1 and W_2 gm of two substances are produced at two electrodes by passing the same quantity of electricity Q through them. Then

$$\frac{W_1}{W_2} = \frac{E_1}{E_2} \qquad \ldots (\text{XX}.2)$$

where E_1, E_2 are their respective chemical equivalents.

To illustrate: If solutions of HCl, $AgNO_3$, $CuSO_4$, etc. be taken in voltameters in the same circuit (see Fig. XX.2) then by the passage of same quantity of electricity (really 96500 coulombs) if 1.008 gm of H_2 be evolved at one electrode, then the quantities of other substances produced at other electrodes will be 35.5 gm chlorine, 107.88 gm Ag, 8 gm oxygen, 31.75 gm Cu, etc. These are their respective chemical equivalents. Now, from the first law, we have

$$W_1 = z_1Q \quad \text{and} \quad W_2 = z_2Q$$

or $\frac{W_1}{W_2} = \frac{z_1}{z_2}$, where z_1, z_2 are their electrochemical equivalents.

$$\text{Hence, } \frac{E_1}{E_2} = \frac{z_1}{z_2}; \text{ i.e. } E \propto z \qquad \text{. . . (XX.3)}$$

The chemical equivalent of an element is proportional to its electrochemical equivalent.

If E and z are the chemical equivalent and electrochemical equivalent of an element respectively and if E_H and z_H are those for hydrogen, then

$$\frac{E}{E_H} = \frac{z}{z_H}; \text{ or } z = \frac{E}{E_H} \times z_H \qquad \text{. . . (XX.4)}$$

for hydrogen, $E_H = 1.008$ and $z_H = 0.0000104$

∴ electrochemical equivalent of an element

$$= \frac{E}{1.008} \times 0.0000104 \approx E \times 0.0000104 \qquad \text{. . .(XX.5)}$$

∴ *Electrochemical equivalent of an element = chemical equivalent of an element × electrochemical equivalent of hydrogen.*

Again, from the 1st Law, $W \propto Q$, when E (chem. eqv.) is constant and from the 2nd Law, $W \propto E$, when Q is constant.

Hence $W = k.QE$, when Q and E vary independently, k is a constant. . . . (XX.6)

If 1 gm-equivalent of a substance is produced by electrolysis, $W = E$.

$$\text{Hence, } E = kQE, \text{ or } Q = \frac{1}{k}$$

That is, *the quantity of electricity required to produce one gm-equivalent of any substance is the same.* This quantity of electricity which produces 1 gm-equivalent of a substance by electrolysis is called a **Faraday**, denoted by F.

$$\text{For a gm-equivalent, } Q = F = \frac{1}{k}, \text{ or } k = \frac{1}{F}$$

$$\text{Substituting in eqn. (XX.6)., } W = \frac{QE}{F} = \frac{EIt}{F} \qquad \text{. . . (XX.7)}$$

$$\text{From eqns. (XX. 1 and XX.7), } W = zQ \text{ and } W = \frac{QE}{F}$$

$$\text{so that } F = \frac{E}{z}$$

F is a constant, it is the quantity of electricity required to produce 1 gm equivalent of an element.

$$\therefore F = \frac{E_1}{z_1} = \frac{E_2}{z_2} = \frac{E_3}{z_3}$$

Both E and z of an element can be very accurately experimentally determined. So, the value of F can be computed.

TABLE

Element	*Eqv. wt.* (E)	*Electrochemical Eqv.* (z)	$F = E/z$ *Coulombs*
Hydrogen	1.008	0.0000104	96496
Silver	107.88	0.001118	96495
Copper	31.78	0.0003294	96494
Oxygen	8.00	0.0000829	96495

$\therefore$ One Faraday, $F \approx 96500$ coulombs

Hence equation XX.7, may be expressed as $W = \dfrac{EIt}{96500}$ ...(XX.8)

The accuracy of Faraday's laws is so high that an estimate of the amount of the chemical change in an electrolyte is used for measuring the amount of electricity flowing. An electrolytic cell inserted in a circuit for this purpose is called a *coulometer*. The silver coulometer is extensivly used. A Pt-basin, carefully dried and weighed, is used as the cathode in which a solution of (approximately 15%) $AgNO_3$ is taken. In the solution is suspended from above a thin anode of pure silver foil. The current is passed for about half an hour. Silver is deposited on the basin. The current is switched off. The basin is washed several times with pure distilled water, dried and weighed again to obtain the weight (W) of Ag deposited. Since z for silver is 0.001118, the quantity of electricity transferred $Q = W/z$ is known. Copper-coulometer, gas-coulometers or iodine coulometers are also used for this purpose.

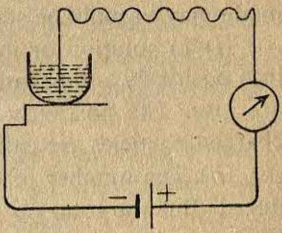


Fig. XX.3
Silver coulometer

On the other hand, Q can be measured from the ammeter and a stop-watch. From Q and W, the electrochemical equivalent can be determined.

Example 1: A current was passed through acidulated water and a copper sulphate solution. 203 c.c. hydrogen at N.T.P. and 0.571 gm copper were deposited. Calculate the eqv. wt. of copper.

$$203 \text{ c.c. hydrogen} = \frac{203}{11200} \text{ gm-eqv. of hydrogen} = \frac{203 \times 1.008}{11200} \text{ gm } H_2$$

$$\text{Now} \quad \frac{W_{Cu}}{W_{H_2}} = \frac{E_{Cu}}{E_{H_2}}$$

$$\text{or} \quad \frac{0.571}{1.008 \times 203/11200} = \frac{E_{Cu}}{1.008}, \quad \text{or} \quad E_{Cu} = \frac{0.571 \times 11200}{203}$$

$$= 31.51$$

Example 2. A current is passed through acidulated water and the solution of the sulphate of the metal M. The volume of H_2 liberated is 9.87 litres and the weight of metal deposited is 28 gm. The specific heat of the metal is 0.093. Find the formula of the sulphate.

$$\frac{E_M}{E_H} = \frac{W_M}{W_H}, \quad \text{or} \quad \frac{E_M}{1.008} = \frac{(9.87/11.2)\text{ gm}}{28\text{ gm}}$$

whence, the eqv. wt. of the metal, $E_M = 31.78$

If x be the valency of the metal, then atomic wt $= 31.78x$

$\therefore 31.78x \times 0.093 = 6.4$ (Dulong-Petil-Law)

whence $x \approx 2.1 = 2$. The metal is bivalent.

$\therefore$ The formula of the sulphate will be MSO_4.

20.3. Arrhenius Theory of Electrolytic Dissociation

Attempts to explain the behaviour of electrolytes in conducting electricity had been made by various investigators since the time of Faraday. But a clear picture of the mechanism of the flow of electricity through electrolytes and the consequent electrolysis was presented first by Arrhenius (1887). The basic postulates of the theory which Arrhenius proposed with a few modifications subsequently made may broadly be stated as follows:

(*i*) In solution or in molten state, the molecules dissociate partly or wholly into positively and negatively charged particles. These electrically charged particles are *ions*. The positively charged particles are called *cations* and the negatively charged particles are called *anions*.

(*ii*) The number of cations may not be equal to the number of anions produced. But the total positive charge carried by the cations must be equal to the total negative charge carried by the anions. The electrolyte as a whole is electroneutral. The cations and anions may be atoms or radicals carrying charge. The properties of ions are different from those of the neutral atoms from which they are produced.

$$NaCl = Na^+ + Cl^- \qquad FeCl_3 = Fe^{+++} + 3Cl^-$$
$$H_2SO_4 = 2H^+ + SO_4^{--} \qquad NH_4NO_3 = NH_4^+ + NO_3^-$$

We now know that electrons are the smallest negatively charged constituent of every atom. Cations are formed when an atom gives away one or more electrons. Anions are formed by acceptance of one or more electrons.

For example,

$$K - e^- = K^+ \qquad Ca - 2e^- = Ca^{++}$$
$$Cl + e^- = Cl^- \qquad S + 2e^- = S^{--}$$

(*iii*) The ions are responsible for carrying electricity through the electrolyte. When the electrodes are connected to the terminals of a battery, *i.e.* the electrolyte is subjected to a potential gradient, the positively charged cations move towards the negative electrode or cathode. And the negatively charged anions move towards the positive electrode or anode.

When the cations reach the cathode, they accept the electron (s) from the cathode and are neutralised.

Similarly, when the anions reach the anode they give up electron (s) to the anode and are neutralised. This explains why the electrolysis is observed at the electrodes and not throughout the solution.

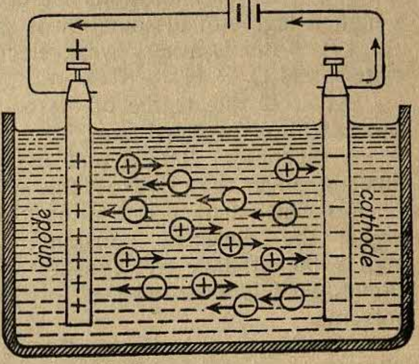


Fig. XX-4. Conduction of electricity in a solution

Copper ions (Cu^{++}) are discharged at the cathode and are transformed into neutral copper atoms there. Chloride ions (Cl^-) are discharged at the anode and become neutral chlorine atoms (subsequently molecules).

The cations thus help in transferring the electrons from the cathode to the electrolyte and anions help in transferring the electrons from the electrolyte to the anode. Although the cations and anions move in opposite directions, both assist in transferring electrons in the same direction from cathode to anode through the electrolyte. The electricity is thus conducted by the charged material particles, the ions. The current is said to flow from anode to cathode, but, in fact, the electrons flow from the cathode to the anode. This is the mechanism of the flow of electricity through an electrolyte.

(*iv*) Apart from the solvent and the temperature, the conducting power or conductance of an electrolytic solution depends upon (*i*) the charge carried by the ions, (ii) the number of ions and (*iii*) the velocity of the ions. That is why two electrolytes taken in the same medium at the same temperature in equal concentrations have different conductances. Thus,

(*a*) 0.1 M HCl has a much higher conductivity than 0.1 M NaCl solution because H^+ ions are much more mobile than Na^+ ions.

(*b*) 0.1M HCl has a much higher conductivity than 0.1M CH_3COOH because the former has much larger number of H^+ ions than that in the latter in equal volumes.

(*v*) **Strong and weak electrolytes:** Many electrolytic substances remain practically completely dissociated at all concentrations. *Examples*: HCl, H_2SO_4, HNO_3, NaOH, KOH, etc. and all salt solutions. These are called *strong electrolytes.* It is now known that the salts exist as ions even in the solid crystalline state. But the crystals do not conduct electricity as the ions occupy fixed positions and cannot move.

On the other hand, many acids and bases are only partly dissociated into ions in solution. *Exampels:* CH_3COOH. H_3BO_3, H_4SiO_4, HCN, NH_4OH, RNH_2 (amines), etc. These are called *weak electrolytes.* There will always be ions as well as undissociated molecules in the solution of a weak electolyte.

$$CH_3COOH \rightleftharpoons CH_3COO^- + H^+; \quad NH_4OH \rightleftharpoons NH_4^+ + OH^-$$

(*a*) In a weak electrolyte the ions have also a tendency to reunite and form the undissociated molecule. There always exists a state of equilibrium between the ions and the undissociated molecules.

(*b*) The extent or degree of dissociation of a weak electrolyte depends upon dilution. The degree of dissociation increases with dilution.

(*c*) When two solutions are taken at the same concentration, one which has a higher degree of dissociation is said to be *stronger* than the other.

(*d*) Water is a very weak electrolyte; one out of 1 million molecules dissociates as $H_2O \rightleftharpoons H^+ + OH^-$.

At 25°C the degree of dissociation (α) of acetic and hydrocyanic acid at a concentration of 0.1M are

α (acetic) = 0.0363 and α (hydrocyanic) = 0.00027, hence acetic acid is much stronger than hydrocyanic acid.

(*e*) The extent of ionisation also depends upon the nature of the solvent. The higher the 'dielectric constant', the greater is the ionisation. Water has a high value of dielectric constant (D = 80), hence it helps ionisation to a large extent. HCl is a strong electrolyte in water but a weak electrolyte in organic solvents,

(*f*) *Degree of ionisation*: Let λ_v be the conductance of an electrolyte when the dilution is v (or conc. C). Other conditions remaining unaltered, the conductance would depend upon the number of ions, and hence on the fraction of the electrolyte which has dissociated. That is, $\lambda_v \propto \alpha C$, where α is the degree of dissociation. At very high or infinite dilution, all the molecules of the electrolyte are dissociated; *i.e.*, $\alpha = 1$. Hence, the conductance at infinite dilution, $\lambda_0 \propto C$.

$$\therefore \quad \frac{\lambda_v}{\lambda_0} = \frac{\alpha C}{C} = \alpha \qquad \ldots \text{(XX.9)}$$

So, the degree of dissociation (α) of a weak electrolyte can be obtained from a knowledge of the conductance at the given dilution and at infinite dilution.

20.4. Avogadro number, N_0

The negative charge carried by an electron has been independently determined by Millikan (1910). The negative charge of an electron, $e = 1.6 \times 10^{-19}$ coulomb. This is the unit of electronic charge in which the charge on all ions are expressed.

When the hydrogen atom loses its only electron, it is transformed into a hydrogen ion, H^+; $H - e^- = H^+$.

The positive charge of the hydrogen ion therefore is also 1.6×10^{-19} coulombs. The charge carried by a Fe^{+++} ion would be 4.8×10^{-19} coulombs.

Now, by Faraday's law, 96500 coulombs are required to discharge 1 gm-eqv. of hydrogen. From dissociation theory, 1 gm-eqv. of hydrogen is formed at the cathode from 1 gm-eqv. of H^+ ions.

Again, 1 gm-eqv. of H^+ ions contains Avogadro number of ions, i.e. N_0 ions. The charge associated with N_0 ions = $N_0 e$.

Hence, $N_0 e$ = one Faraday = 96500 coulombs.

$$\text{or, Avogadro number, } N_0 = \frac{F}{e} \approx \frac{96500 \text{ coulombs}}{1.6 \times 10^{-19} \text{ coulombs}} \approx 6.02 \times 10^{23}$$

Conversely, the Avogadro number has also been independently determined and found to be $N_0 = 6.02 \times 10^{23}$. Accepting this value, the charge of an electron can be computed:

$$e = F/N_0 = 96500/(6.02 \times 10^{23}) = 1.6 \times 10^{-19} \text{ coulombs.}$$

20.5 Evidence in support of the Arrhenius Theory

(*i*) *Colligative properties*: Immediate support to Arrhenius theory of electrolytic dissociation came from the colligative properties of dilute solutions of electrolytes, such as, osmotic pressure, boiling-pt. elevation, etc.

The solutions of non-electrolytes obey the van't Hoff relation, say, $\pi = CRT$. But with electrolyte solutions, the observed osmotic pressure is much higher. Van't Holf simply expressed this deviation by a factor *i*, such that $\pi_{obs} = i.\pi_{calc.} = i\,CRT$. Identical deviations were found when other colligative properties were measured with the given solution.

It was logically argued that at a constant temperature, higher values of osmotic pressure (π) must be due to an increase in concentration (C), *i.e.*, the number of particles present in solution of the electrolyte.

Arrhenius suggested that this was due to the dissociation of a fraction of the electrolyte molecules giving a higher total of individual particles in solution, the ions having separate entities. Hence

$$\pi_{obs} = [1 + (n-1)\alpha]CRT = iCRT$$

where α is the degree of dissociation, and n is the number of ions produced from each molecule (see Sec. 14.19).

$$\therefore \quad i = 1 + (n-1)\alpha, \quad \text{or} \quad \alpha = \frac{i-1}{n-1} \qquad \ldots \text{(XX.10)}$$

The degree of dissociation obtained from conductivity results (eqn. XX.9) was found in good agreement with the values obtained independently from colligative properties (XX.10). This demonstrates the correctness of the theory of electrolytic dissociation.

(*ii*) *Crystal structures:* X-rays studies of the crystal lattices have revealed that solid salts are built up of ions and not of molecules. A crystal of sodium chloride is not an aggregation of NaCl-molecules but are formed of equal numbers of Na^+-ions and Cl^--ions. Since in the crystalline form the ions cannot move about and so they cannot conduct electricity in the solid state.

(*iii*) *Ionic reactions:* When $AgNO_3$ solution is added to the solution of *any* chloride salt, always the same white precipitate of AgCl is obtained.

$$K^+ + Cl^- + Ag^+ + NO_3^- \rightarrow K^+ + NO_3^- + AgCl$$

This is possible only if we assume this as an ionic reaction between Ag^+ and Cl^- ions. If $AgNO_3$-solution be added to chloroform ($CHCl_3$), no ppt. is obtained as chlorine is not present as Cl^--ion. Every precipitation reaction in inorganic chemistry has the same explanation.

(*iv*) *Colours of salt solutions:* KCl solution is colourless indicating K^+ and Cl^--ions have no colour. But $KMnO_4$ solution is pink, and in fact, every permanganate solution has a pink colour. This indicates that MnO_4^--ion has the pink colour. Similarly, every ferric salt solution is yellow, as the Fe^{3+}-ions have yellow colour. These give support to the concept of ionisation of electrolytes.

(*v*) *Heat of neutralisation:* The heat of neutralisation of a strong acid by any strong alkali is always the same, and about 13.6 kcal. This is possible only if both the strong acids and bases are completely dissociated (see Sec. 9.6).

The various laws, such as Ostwald dilution law, etc. indirectly confirms the theory of dissociation.

20.6. Electrolytic dissociation and thermal dissociation

The electrolytes, even the weaker ones, dissociate into ions and the ions have also the tendency to unite to form undissociated molecules. This is electrolytic dissociation.

Certain substances dissociate into two or more molecules on application of heat; the products however unite when these are cooled. This is thermal dissociation.

$$NH_4Cl \rightleftharpoons NH_4^+ + Cl^-; \text{ (electrolytic dissociation)}$$
$$NH_4Cl \rightleftharpoons NH_3 + HCl; \text{ (thermal dissociation)}$$

(*i*) Both thermal and electrolytic dissociations are reversible, i.e. proceed in both directions. There is an equilibrium between the products of dissociation and the undissociated molecules.

(*ii*) In thermal dissociation, the products are neutral molecules and the products can be isolated. In electrolytic dissociation, the products are charged ions and the ions cannot be isolated from one another.

(*iii*) In thermal dissociation no medium is necessary. But in electrolytic dissociation very often a suitable medium is required.

(*iv*) Both thermal and electrolytic dissociation depend on temperature, but the influence of temperature on electrolytic dissociation is relatively less.

MIGRATION OF IONS

The movement of ions in an electric field can be easily demonstrated by simple experiments. In a tube as shown in Fig. 4a, the horizontal portion is filled up with a set jelly of agar-agar containing a trace of NaOH and a little phenolphthalein so that the jelly is pink in colour. The two vertical limbs are filled up with dil. H_2SO_4 and with dil. $ZnSO_4$ solution. The anode is inserted in the acid solution and the cathode in the zinc sulphate solution. On switching the current, H^+ ions move towards the anode through the jelly neutralising progressively the alkali. In consequence, the pink colour also progressively disappears. The movement of the pink boundary in the jelly confirms the motion of the H^+ ions.

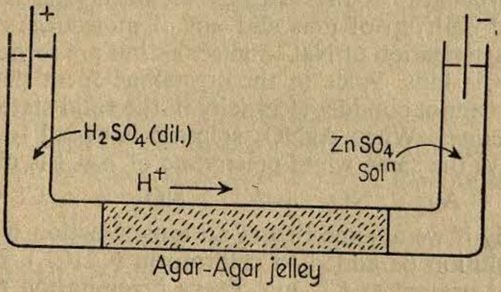


Fig. 4a

20.7. Transport numbers

Under a potential gradient, current is transported by ions, the positive ions moving towards the cathode and negative ions towards the anode. The total charge released at the cathode and at the anode are of course equal but the fraction of the total current conveyed by the cations and the anions through the solution are not necessarily equal. For example, in a dilute solution of nitric acid, only 16% of the current is conveyed by NO_3^- ions, the rest by the H^+ ions. In a dilute copper sulphate solution, Cu^{++} ions transport 38% of the current and SO_4^{--} ions transport 62%. The transport of current by ions in a solution depends not only upon the charge and number of the ions but also on the speed of the ions. It is obvious that having same charge the ions with greater speed will pass a section of the solution in greater numbers than those with a lower speed. Hence the former would transport a larger amount of current. A relation between the speed of an ion and the fraction of current conveyed by it may be obtained in the following way.

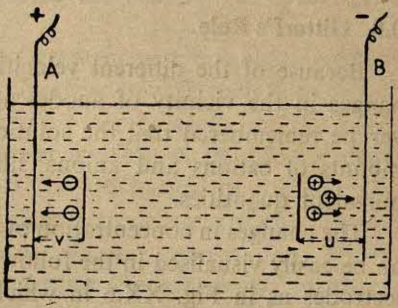


Fig. XX.5

Let us take an electrolyte between two electrodes *A* and *B* as in Fig. XX.5. Let the number of cations per c.c. of the solution be n_+ each carrying a charge z_+. Suppose the current passing through the solution be *I* under a potential difference of *E* volts. Further suppose that *u* and *v* are the velocities of the cation and anion respectively under this voltage. Consider now only unit cross-section of the two electrodes, when the current passes just for one second. It is evident that all the anions which are within a distance *v* from the anode would reach *A* and during this time all the cations within a distance *u* from the cathode would reach *B*. Remembering unit cross-section, the number of cations and anions to be discharged on *B* and on *A* are n_+u and n_-v respectively. If the quantity of electricity associated with unit charge be represented by *e* then

the current carried by cations, $I_+ = (n_+u)z_+.e$

and the current carried by anions, $I_- = (n_-v))z_-.e$

The total current carried by the cations and anions together,

$$I = I_+ + I_- = n_+z_+\,e.u + n_-z_-e.v \qquad \ldots (XX.11)$$

$$= n_+z_+e.u + n_+z_+e.v$$

the solution being electrically neutral, $n_+z_+ = n_-z_-$

It may be remembered that though physically the ions migrate in opposite directions, these help the passage of current in the same direction.

The fraction of the current carried by cations and anions, represented by t_+ and t_-, are called *transport* or *transference* numbers. These would be,

(*a*) $$t_+ = \frac{I_+}{I} = \frac{n_+z_+eu}{n_+z_+eu + n_+z_+ev}$$

or transference number of cation, $t_+ = \dfrac{u}{u+v}$ ... (XX.12)

and (*b*) $$t_- = \frac{I_-}{I} = \frac{n_-z_-ev}{n_+z_+eu + n_+z_+ev}$$

$$\text{or transference number of anion,}\quad t_- = \frac{v}{u+v} \qquad \ldots \text{(XX.13)}$$

$$\text{Further,}\quad t_+ + t_- = 1;\ \text{ and }\ \frac{t_+}{t_-} = \frac{u}{v} \qquad \ldots \text{(XX.14)}$$

20.8. Hittorf's Rule

Because of the different velocities of anions and cations, the concentration changes in the vicinity of anodes and cathodes are also different. It must however be remembered that the solution as a whole is always neutral and that amounts of cations and anions liberated at the respective electrodes are in equivalent quantities.

The changes in concentration of the electrolyte near the cathode and the anode can be easily visualised in the following way. Consider an electrolyte between two electrodes as in Fig. XX.6 in which positive and negative ions are represented by + and – signs.

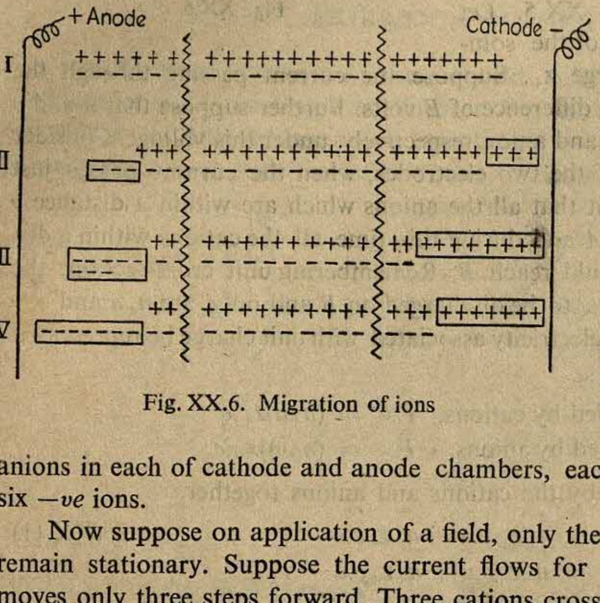


Fig. XX.6. Migration of ions

Before the passage of current, the condition of the ions are as shown in I of the figure. An equal distribution of $+ve$ and $-ve$ ions is present everywhere. Let us imagine the cell divided into three chambers by two partitions shown by serrated lines, so that we have a cathode chamber, a central chamber and an anode chamber. Let us also take equal number of cations and anions in each of cathode and anode chambers, each having say, six $+ve$ and six $-ve$ ions.

Now suppose on application of a field, only the cations move but the anions remain stationary. Suppose the current flows for such time that every cation moves only three steps forward. Three cations cross each partition, so that there are three excess cations in cathode chamber and three excess anions in the anode chamber. This is represented in II. Since each compartment should be electrically neutral, so three cations are discharged on the cathode and three anions on the anode. It is thus seen that though the anions did not move, yet these were discharged in amounts equivalent to that of the cations. Moreover, the motion of the cations caused a fall in the concentration of electrolyte in the anode chamber. The anions did not move and hence the concentration in the cathode chamber remained unaltered.

In the next case III, let us consider that both anions and cations are moving at equal rate, say each ion moves four steps in its respective direction in a given time. At the end of this time interval, there shall be eight excess anions in the anode chamber and eight excess cations in the cathode chamber, all of which would be discharged as the solution in both chambers had to be electrically neutral. We now find that when the speeds of both ions are the same, the fall in concentration in both the anode and the cathode chambers is also equal. The amount of ions discharged at each electrode is proportional to the sum of the speeds of the two ions.

Now let us suppose cations and anions are moving with unequal speeds. Suppose each cation moves four steps and each anion three steps in their respective directions in a given interval of time. The condition is represented in IV. The excess anions would be seven in the anode chamber and the excess cations also seven in the cathode chamber. These ions would be discharged at the corresponding electrodes. The amounts discharged at each electrode are not only equal but also proportional to the sum of the speeds of the two opposite ions. This means that *Faraday's laws will hold whatever be the ratio of the ionic speeds.* Further the fall in concentration in the anode chamber is proportional to the speed of cations. The fall in concentration in the cathode chamber is proportional to the speed of anions. It is also seen that the concentration in the central chamber remains unaffected.

We are thus led to the conclusion that due to passage of a current,

$$\frac{\text{No. of equivalents of electrolyte lost from anode compartment}}{\text{No. of equivalents of electrolyte lost from cathode compartment}}=\frac{u}{v}$$

Further, $$\frac{\text{No. of equivalents of electrolyte lost from anode compartment}}{\text{Total no. of equivalents deposited at each electrode}}=\frac{u}{u+v}=t_+$$

and $$\frac{\text{No. of equivalents of electrolyte lost from cathode compartment}}{\text{Total no. of equivalents deposited on each electrode}}=\frac{v}{u+v}=t_- \qquad \ldots \text{(XX.15)}$$

This is *Hittorf's rule.*

It is often used in determining the transference number of ions. Fig. XX.7 shows one of the simplest type of transference number tube used in Hittorf's method. It consists of tubes *A* and *B* as the cathode and anode chambers with the intervening *C* as the middle portion. Every section is provided with a stop cock at the bottom for withdrawing the solution. Electrodes are inserted through corks at the top. In the circuit in series are connected a milliammeter (*M*), a silver coulometer (*X*), and a resistance (*R*). The transport number tube (*ACB*) is filled with the electrolyte under examination. A current of 20 milliamperes or so is then passed for three hours so that concentration changes are appreciable. In the silver coulometer is taken a solution of (approximately) *N*/10 $AgNO_3$. From the silver deposited on the Pt-basin of the coulometer, the equivalent

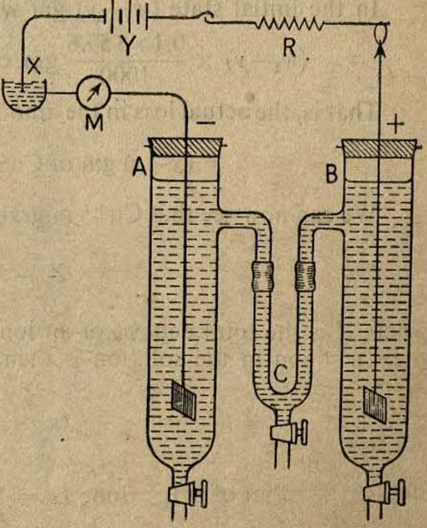


Fig. XX.7. Transference number detn. by Hittorf's method

of current passed or the equivalents of ions deposited in the other electrodes in the circuit are accurately known (Faraday's laws).

Since it is required to measure the concentration change due to migration of ions, adequate precautions are taken to prevent diffusion, convection or mechanical disturbance of the solution. When the current is stopped, the solution is drained out from one or both the chambers, weighed and then analysed. The loss or gain in concentration of the electrolyte in the chambers is known and is expressed in terms of equivalents for a definite *weight* of the solvent. From these the transference number can be easily computed. Let us illustrate this with a solution of copper sulphate.

Suppose initially the Hittorf tube is filled with a 0.1 molal solution of copper sulphate and electrolysed between copper electrodes.

After electrolysis, let the amount of solution taken out from the cathode chamber be w_1 gm, which, on analysis (iodometrically), was found to contain w_2 gm of copper.

Further suppose, the increase in weight of the cathode in the coulometer due to deposit of silver be w_3 gm.

(The equivalent weight of Ag = 107.88, mol. wt. of copper sulphate = 159.6)

It is evident that the total quantity of electricity passed is given by w_3 gm of silver, *i.e.*,

$$\frac{w_3}{107.88} \text{ equivalents } = Z \text{ faradays (say).}$$

In the cathode chamber then Z equivalents of copper must have been deposited, But the loss in the concentration in this chamber would be less than Z, for other Cu^{++} ions have meantime migrated into this chamber.

$$\text{Now } w_2 \text{ gm of copper} \equiv w_2 \times \frac{CuSO_4}{Cu} \equiv w_2 \times \frac{159.6}{63.5} \equiv 2.512w_2$$
$$\equiv y \text{ gm of } CuSO_4 \text{ (say)}$$

That is, the cathode solution analysed contained (w_1-y) gm of water.

In the initial state (w_1-y) gm water was associated with

$$(w_1-y) \times \frac{0.1\times159.6}{1000} \text{ gm of copper sulphate } = x \text{ gm (say).}$$

That is, the actual loss in the amount of copper sulphate in the cathode solution

$$= (x-y) \text{ gm of } CuSO_4 = \frac{(x-y)\times2}{159.6} \text{ equivalents}$$

We can now see that Cu^{++} migrating into the cathode solution

$$= Z - \frac{2(x-y)}{159.6} \text{ equivalents}$$

where Z is the total deposit of an ion in equivalents. The transference number of the Cu^{++} ion in the solution is then

$$t_+ = \frac{Z-[2(x-y)/159.6)]}{Z}$$

and that of SO_4^{--} ion, $t_- = 1 - t_+ = \dfrac{2(x-y)/159.6}{Z}$

Example 3. A solution of $AgNO_3$ containing 1.06 mg of silver per gram of the solution was electrolysed between silver electrodes. The anode liquid after electrolysis contained 42.94 mg silver in 25 gm of the solution. In a copper coulometer in series 9.146 mg of copper were deposited. Calculate the transport numbers of Ag^+ and NO_3^- ions. [Cu = 63.5, Ag = 108] (Rajasthan Univ. '69).

Before electrolysis,

the amount of Ag contained in 25 gm solution $= 25 \times 0.00106$ gm

$= 0.0265$ gm

After electrolysis, 25 gm solution contained $= 42.94$ mg $= 0.04294$ gm

$\therefore$ Increase in Ag-content around anode $= 0.04294 - 0.0265$ gm

$= 0.01644$ gm Ag

From the anode compartment, Ag migrated out, yet there is an increase. This is due to the dissolution of Ag from the Ag-electrode.

From the Copper-coulometer, copper deposited = 9.146 mg.

Hence, from Faraday's 2nd Law, the amount of silver dissolved x is given by,

$$\frac{x}{9.146} = \frac{108}{31.75} \quad \text{or} \quad x = 0.0311 \text{ gm}$$

Hence, the amount of Ag migrating out from the anode comparment $= 0.0311 - 0.01644 = 0.01466$ gm Ag

$$\text{Hence} \qquad t_{Ag^+} = \frac{\text{Loss of Ag in anode compartment}}{\text{Total silver deposited or dissolved on the electrode}}$$

$$= \frac{0.01466}{0.0311} = 0.471$$

$$\text{and} \qquad t_{NO_3^-} = 1 - 0.471 = 0.529$$

20.9. Moving Boundary Method

In this method, the transference number is determined by directly following the speeds of ions under an applied potential. A device is made in which the boundary between two ionic solutions is clearly distinguishable. By passing a suitable current the boundary is made to move in a desired direction. The measurement of transfer of the boundary enables one to calculate the transference number. A diagrammatic sketch of the apparatus used is given in Fig. XX.8.

The vertical tube PQ is the electrolytic cell. This has a narrow but uniform bore, which is carefully measured. Suppose the transference numbers of the ions of MA (say HCl) are to be determined. The solution of MA is placed in the tube between two *indicator*

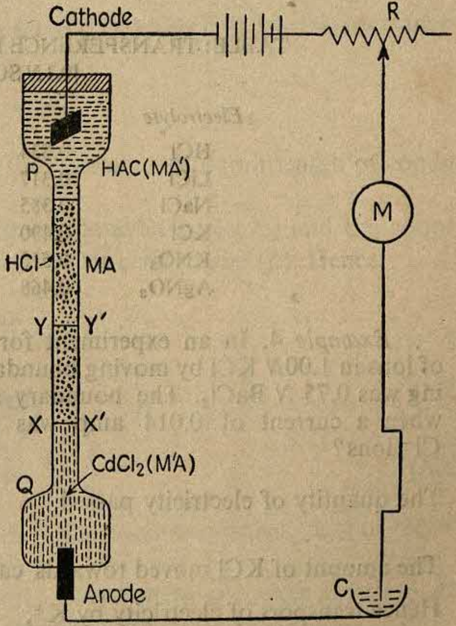


Fig. XX.8. Transference number by moving boundary method

solutions M′A and MA′, one having common anion and another having common cation with the given electrolyte, say $CdCl_2$ and HAc, as shown. The three solutions are taken in increasing density downwards so that mixing is avoided. The indicators (M′A and MA′) are so chosen that the speed of M′ is less than that of M, and the speed of A′ is less than that of A. Here, Cd^{++} has a lower speed than that of H^+, and the speed of Ac^- is less than that of Cl^-. The lower part of the tube is filled with $CdCl_2$ solution with a Cd-anode in it. A pt-cathode is inserted at the top in the HAc solution. The circuit also contains a coulometer (*C*), milliammeter (*M*) and a resistance (*R*). The junction of the HCl and $CdCl_2$ solution is quite sharp and distinguishable. The current is next switched on. The H^+ ions move upwards, much faster than the Cd^{++} ions following. The result is that the boundary slowly moves upwards from *xx′* to *yy′* during the period (*t*) of electrolysis. The displacement (*l*) of the boundary is accurately measured by a cathetometer.

If the cross section of the tube be '*a*', then the volume swept out by the boundary in moving from *xx′* to *yy′* is ($l \times a$) c.c. If *c* be the concentration of the HCl solution, the amount of acid moved upwards during the experiment is $lac/1000$ gm-equivalents.

If *Q* faradays of electricity have been passed during electrolysis, known from the coulometer, then the fraction of the current transported by H^+ ions is t_+Q faraday. Hence, t_+Q gm-equivalent H^+ ions have migrated.

$$\therefore \quad t_+Q = \frac{lac}{1000}, \quad \text{or} \quad t_+ = \frac{lac}{1000Q} \qquad \ldots (XX.16)$$

$$\text{Since} \quad Q = It/F; \quad \text{hence} \quad t_+ = lacF/(1000It) \qquad (XX.17)$$

TABLE: TRANSFERENCE NUMBERS OF CATIONS (25°C)
[0.1*N* SOLUTIONS]

Electrolyte	t_+	*Electrolyte*	t_+
HCl	0.834	NaOH	0.183
LiCl	0.317	KOH	0.265
NaCl	0.385	$CuSO_4$	0.373
KCl	0.490	$CdSO_4$	0.364
KNO_3	0.510	KI	0.492
$AgNO_3$	0.468	KBr	0.492

Example 4. In an experiment for the determination of transport numbers of ions in 1.00*N* KCl by moving boundary method, the indicator electrolyte following was 0.75 *N* $BaCl_2$. The boundary swept a volume of 0.1200 c.c. in 1670 sec when a current of 0.014 amp was passed. What is the transport number of Cl^- ions?

The quantity of electricity passed, $Q = \dfrac{0.014 \times 1670}{96500}$ faradays

The amount of KCl moved towards cathode $= \dfrac{0.1200 \times 1.00}{1000}$ equivalents

Hence transport of electricity by K^+,

$$t_+ = \frac{0.1200 \times 96500}{1000 \times 0.014 \times 1670} = 0.495$$

$\therefore$ Transport number of Cl^- ions, $t_- = 1 - t_+ = 0.505$

Example 5. In a moving boundary experiment for determination of transport number of Na^+ ion in 0.02 M NaCl using $CdCl_2$ solution as indicator-electrolyte, the boundary moved through a distance of 7 cm in 2414 seconds with 0.0016 amperes. The cross section of the tube was 0.115 cm². Calculate the transport number of Na^+ ion.

$$t_+ = \frac{lac\,F}{1000.I.t} = \frac{7\times0.115\times0.02\times96500}{1000\times0.0016\times2414} = 0.4023$$

Abnormal transport numbers: The transport numbers determined experimentally are sometimes found to be abnormally low. For example with very dilute solutions of CdI_2 the transport number $t_{Cd^{++}}$ is normal, but with increase in concentration, the value decreases to a large extent.

Transport numbers of Cd^{++} ions at various concentrations (18°C)

Conc.	0.01	0.02	0.05	0.10	0.50 *N*
t_+	0.444	0.442	0.396	0.296	0.003

This can be explained only by assuming the formation of complex ions of cadmium. $2CdI_2 \rightleftharpoons Cd^{++} + [CdI_4]^{--}$ That is, the postively charged Cd^{++} migrating towards the cathode is much less. Such behaviour is also noticed with other complex formations.

CONDUCTANCE OF SOLUTIONS

20.10. Specific and Equivalent Conductances

In a metallic conductor of length (l) and cross-section (a) the resistance (R) is given by

$$R = \rho\frac{l}{a}$$

where ρ is the specific resistance. It is the resistance of a unit length of conductor of unit cross-section.

The reciprocal of resistance is termed 'conductance' ($\wedge$) and the reciprocal of specific resistance, the *specific conductance* or *conductivity* (L). Hence,

$$\text{the specific conductance,} \quad L = \frac{1}{\rho}$$

$$\text{The conductance of a given solution, } \wedge = \frac{1}{R} = \frac{1}{\rho}.\frac{a}{l} = L\frac{a}{l} \quad \ldots\text{(XX.18)}$$

$$\therefore \quad L = \frac{1}{R}.\frac{l}{a} \quad \ldots\text{(XX.19)}$$

The resistance is expressed in units of *ohm*, the conductance has units of *reciprocal ohm* or *mho*.

The conductance of solutions is also governed by the same relations. From XX.18, if $l = 1$, $a = 1$, the specific conductance $L = \wedge$. That is,

the specific conductance (L) *is the conductance of the solution enclosed between two electrodes of* 1 *sq. cm. area and* 1 *cm. apart.*

The conductance of the solution depends upon the number of ions present and hence on the concentration. To compare the conductivity of different solutions, it is necessary to take the concentration of the solutions into consideration. It is done by using equivalent conductance, λ.

The equivalent conductance is defined as the conductance of a solution containing 1 *gm-equivalent of the dissolved electrolyte such that the entire solution is placed between two electrodes* 1 *cm apart.* As direct determination of this quantity would need electrodes of enormous sizes, the equivalent conductance (λ) is always evaluated through measurement of specific conductance (L) with the help of eqn. (XX.19).

Suppose the solution of the electrolyte has a concentration of c gm-eqv. per litre. Then the volume of the solution containing 1 gm-eqv. would be $1000/c$ cubic centimeter. If this volume be imagined to be placed between two electrodes 1 cm apart, ($l = 1$), the cross-section of the column of solution or electrodes would be $1000/c\cdot$ sq. cm. Hence the equivalent conductance of the solution,

$$\lambda = \frac{a}{l} \cdot L = \frac{1000}{c \times 1} \times L = \frac{1000L}{c}, \qquad \ldots (\text{XX.20})$$

L being the specific conductance.

An alternative unit, called *molar conductance*, μ, is defined as the conductance of a solution containing 1 gm-mole per litre, the solution being placed between two electrodes 1 cm apart. As before $\mu = 1000\ L/C'$, where C' is the molar concentration.

20.11. Determination of Conductance

The specific conductance (L) of a solution is always obtained by measuring the resistance (R) of the solution taken in a suitable container of known dimensions, called *conductivity cell*. Various types of conductivity cells are in use, some are shown in Fig. XX.9. These are stoppered glass bottles, inside which there are two similar Pt-electrodes placed at a definite distance fixed through Pt-wires fused to the walls. These wires are led into two arms of the bottle outside containing mercury for easy contact with electric circuit. Inside, the electrodes are placed opposite to each other and are coated with pt-black. The distance (l) between two electrodes in a cell is fixed.

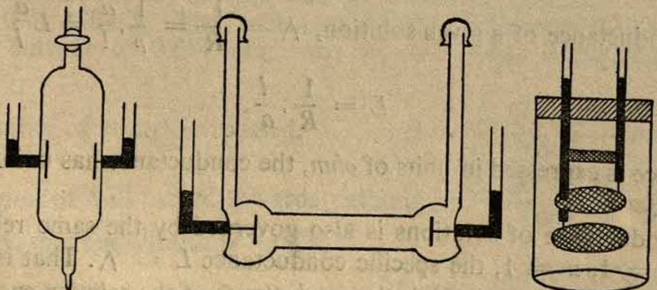


Fig. XX.9. Different types of conductivity cells

The solutions also obey Ohm's law. The resistance of the solution is measured by placing the conductivity cell containing the solution in one arm of a Wheatstone bridge set-up as shown in Fig. XX.10.

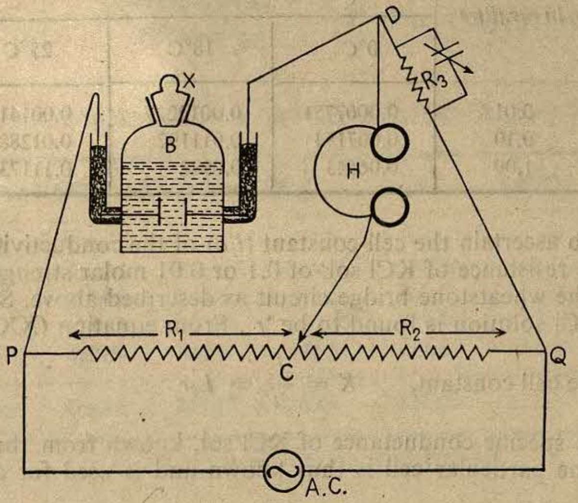


Fig. XX.10. Diagram for conductivity determination circuit

In the experimental arrangement, the solution is taken in the conductivity cell *B* and connected to one arm of the bridge *PD*, the other arm *QD* carries a variable resistance R_3. *PQ* is a uniform slide-wire on which moves a contact point '*C*'. This contact point *C* is connected through an ear-phone to the point *D*, junction of the other two arms *PD* and *QD* containing the cell and the variable resistance R_3. An alternating current (say 1000 cycles) is used in the circuit. The current should be an alternating one as otherwise electrolysis would occur in the cell and concentration would change. The temperature is controlled by keeping the cell partially immersed in a thermostat. The current from the source enters at *P* and *Q* and divides into two parallel branches along *PCQ* and *PDQ*.

Using a definite resistance R_3 in the arm *DQ*, the contact point *C* is moved along the slide-wire until no sound is produced in the earphone, *i.e.*, until no current passes along *DC*. Under this condition, potentials at *C* and *D* are the same, hence

$$\frac{X}{R_3} = \frac{R_1}{R_2} \quad \text{or} \quad X = \frac{R_1}{R_2} R_3 = \frac{l_1}{l_2} R_3$$

where *X* is the resistance of the solution. R_1 and R_2 are the resistances of the two portions of the slide-wire, the ratio arms l_1 and l_2. In fact, the R_1/R_2 is the ratio of the lengths *CP*/*CQ*, when a wire of uniform cross-section is used. The resistance of the solution (*X*) taken in the cell is thus known.

But to know the specific resistance, it would be necessary to determine the cross-section and the distance of the electrodes of the cell used. These determinations are not quite easy. In fact the ration (*l*/*a*) of the cell, called **cell constant (*K*)** is ascertained in an alternative way.

Using conductivity cells of accurately known dimensions (*l* and *a*) Kohlrausch and his co-workers determined very precisely the specific conductance of standard solutions of pure KCl at different temperatures. Some of the values of specific conductances of KCl solutions are quoted below from standard tables.

TABLE: SPECIFIC CONDUCTANCES OF KCl SOLUTIONS

Conc. in eqv./litre	*L in mhos*		
	0°C	18°C	25°C
0.01	0.0007751	0.0012227	0.0014114
0.10	0.007154	0.011192	0.012886
1.00	0.06543	0.0982	0.11173

In order to ascertain the cell-constant (l/a) of the conductivity cell used in the laboratory, the resistance of KCl sol. of 0.1 or 0.01 molar strength is measured in this cell with the wheatstone bridge circuit as described above. Suppose the resistance of the KCl solution is found to be 'r', From equation (XX.19),

$$\text{the cell constant,} \quad K = \frac{l}{a} = L_s r \qquad \text{. . . (XX.21)}$$

where L_s is the specific conductance of KCl sol. known from the Table. The cell-constant for the particular cell is thus known and is used for all measurements with this cell.

For a given solution, the resistance (R) is measured in the usual way with the wheatstone-bridge. The specific conductance (L) of the solution,

$$L = \frac{l}{a}.\frac{1}{R} = K/R$$

Since K and R are both known, the specific conductance of the given solution is also known. The equivalent conductance of the given solution is then obtained with equation (XX.22).

$$\lambda = \frac{1000 \times L}{C}$$

It may be mentioned that in preparing the solutions, 'conductivity water' *i.e.*, highly purified water obtained from repeated distillation in an all quartz apparatus has to be used.

Example 6. The specific conductivity of a $0.1N$ acetic acid solution at 18°C is 0.000471 r.o. and that of a $0.01N$ sodium acetate solution is 0.000781 r.o. What are the equivalent conductivities of the two solutions? (Delhi Univ. '70)

$$\lambda_{\text{HAC}} = \frac{L_{\text{HAC}} \times 1000}{C} = \frac{0.000471 \times 1000}{0.1} = 4.71 \text{ mhos cm}^2/\text{gm eqv.}$$

$$\lambda_{\text{NaAC}} = \frac{L_{\text{NaAC}} \times 1000}{C} = \frac{0.000781 \times 1000}{0.01} = 78.1 \text{ mhos cm}^2/\text{gm eqv.}$$

Example 7. The resistances of a cell containing $0.1N$ KCl and $0.1N$ $AgNO_3$ were 337.62 and 362.65 ohms respectively at 25°C. The sp. conductance of $0.1N$ KCl is 0.01286 ohms^{-1} cm^{-1} at 25°C.

Calculate (*i*) cell constant and (*ii*) equivalent conductance of $0.1N$ $AgNO_3$ solution.

(*i*) Using equation (XX.21), we have the cell-constant,

$$K = L_{\text{KCl}} \times r_{\text{KCl}} = 0.01286 \times 337.62 = 4.344 \text{ cm}^{-1}$$

(*ii*) From eqn. (XX.20), $\lambda_{AgNO_3} = \dfrac{L \times 1000}{C} = \dfrac{K \times 1000}{r_{AgNO_3} \times C}$

$$= \frac{4.344 \times 1000}{362.65 \times 0.1} = 120 \text{ ohms}^{-1} \text{ cm}^2/\text{gm eqv.}$$

TABLE: EQUIVALENT CONDUCTANCES (25°C)

Conc. (*N*)	HCl	NaOH	KCl	NaCl	$AgNO_3$	CH_3COOH
1.000	332.8	—	111.9	—	—	—
0.100	391.32	221.0	128.96	106.74	109.14	5.20
0.010	412.00	237.0	141.27	118.51	124.76	16.20
0.001	421.36	245.0	146.95	123.74	130.51	48.63
0.0005	422.74	246.0	147.81	124.50	131.36	135.0
∞ *-dilution*	426.16	248.1*	149.9	126.45	133.3	391*

*Calculated from ion conductances

Usually, the equivalent conductivity increases with increase in temperature. The conductace of an aqueous solution of an electrolyte increases approximately 2% per °C rise in temperature.

20.12. Equivalent Conductance and Concentration

The table given above clearly shows that the equivalent conductance increases with dilution, especially in the case of weak electrolytes. The effect of dilution on equivalent conductance is considered separately for strong and weak electrolytes.

Strong electrolytes: Solutions of salts like KCl, $CaCl_2$, Na_2SO_4, NaAc, etc. or acids such as HCl, H_2SO_4 etc. have very high equivalent conductance even at ordinary concentrations. With dilution their conductances increase to some extent and ultimately tend to reach a limiting value. The conductance when the solution is infinitely dilute is called the **equivalent conductance at infinite dilution,** denoted by λ_0. It is indeed the value of equivalent conductance reached at very high dilution such that any further dilution would not change it.

Kohlrausch suggested an empirical relation from experimental results between the concentration, c and the equivalent conductance λ_c.

$$\lambda_c = \lambda_0 - b\sqrt{c} \qquad \ldots \text{(XX.23)}$$

where b and λ_0 are constants for a given electrolytic solution. At very low concentration, *i.e.*, at infinite dilution, evidently $\lambda_c = \lambda_0$. The plot of λ *vs.* $\sqrt{c}$ is almost linear for many electrolytes, like, KCl, HCl etc. (Fig. XX.11). Extrapolation of the linear curves to high dilutions, *Lt.c*→0, leads to the value of λ_0, the equivalent conductance at infinite dilution.

The accepted idea is that strong electrolytes (HCl, NaOH, NaAc, KCl) are completely ionised in solution even at oridinary concentrations.

The question to be answered is why then should the equivalent conductance in such solutions of strong electrolytes vary with dilution. The conductance of a solution of a given electrolyte depends upon the number of ions and the speed with which the ions move. In the case of a solution of a strong electrolyte, the ionisation is complete, the number of ions will be the same, for 1 gm-equivalent will produce the same number of ions at all dilutions. Therefore, it is the speed of ions which changes with dilution. In a strong electrolyte, the density of ions is very high; every ion is surrounded by ions of opposite charge. The result is an interionic attraction between ions of opposite character. Such interionic attraction effectively reduces the speed of the ions and hence the equivalent conductance of the solution. When concentration is lowered by increasing the dilution, the ions go far apart and the interionic forces are reduced. The ions would then move more freely. At infinite dilution, the interionic attraction practically disappears and the limiting value of the equivalent conductance is obtained.

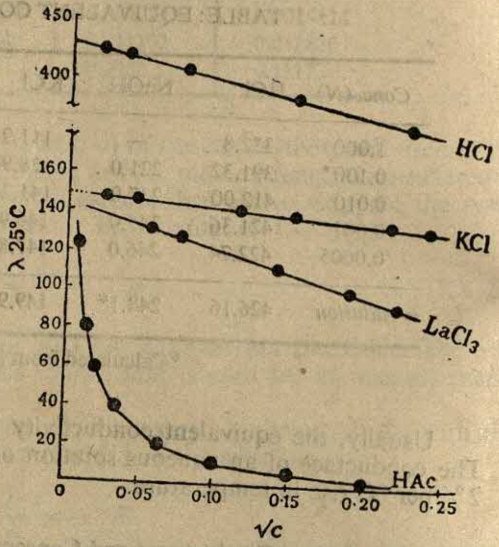


Fig. XX.11. Eqv. conductance versus $\sqrt{C}$

Weak Electrolytes: The equivalent conductance of weak electrolytes such as solutions of ammonia, organic fatty acids etc. is low at ordinary concentrations, say 0.1*N*. With dilution λ_c increases considerably as is shown by the plot of λ_c *vs* $\sqrt{c}$ for acetic acid in Fig. XX.11. It is seen that even when the concentration is made very small, the equivalent conductance rises steeply with dilution. As such it is not possible to reach a limiting value by extrapolation as in the case of strong electrolytes. Further dilution of the solution raises the resistance of the solution which is of the same order as that of water. So the experimental realisation of the limiting value of equivalent conductance at infinite dilution is not possible.

In these electrolytes, the extent of ionisation is small and the number of ions are relatively few. So the interionic attraction between the ions is not of any importance. Whatever ions are produced by ionisation they are free to move, *i.e.*, their speeds are not effected by interionic attraction. In solutions of ordinary concentration, the degree of ionisation is quite small. The increase in equivalent conductance with dilution is due to increase in the degree of ionisation. Therefore, the degree of dissociation (α) for weak electrolytes may be taken as the conductance ratio, $\alpha = \lambda_c/\lambda_0$, as proposed in the Arrhenius theory.

Specific conductance: The effect of dilution on the specific conductance of a solution is opposite to that on equivalent conductance. The specific conductance is the conductance of a centimeter-cube of the solution. With dilution the number of ions present in one cm^3 is reduced and hence the specific conductivity also decreases.

In the case of weak electrolytes, with dilution the degree of dissociation and hence number of ions increases. But this increase is not sufficient to compensate for the loss in number of ions due to dilution. So in all electrolytes, the specific conductance decreases with dilution. The effect is shown in the Table below:

Conc.	*Sp. conductance (L)*		*Eqv. conductance* (λ)	
	KCl	CH_3COOH	KCl	CH_3COOH
1.0	0.0982	0.00132	98.2	1.82
0.1	0.01119	0.00024	111.9	2.30
0.01	0.001225	0.000143	122.5	14.3

20.13. Kohlrausch's Law of Independent Migration of Ions

While investigating the equivalent conductances at infinite dilution (λ_0), Kohlrausch found that when salts of potassium and sodium with a common anion are taken, the difference in their λ_0- values was found to be same irrespective of the nature of the anion. That is, $\lambda_0^{KCl}-\lambda_0^{NaCl}=\lambda_0^{KNO_3}-\lambda_0^{NaNO_3}=\lambda_0^{\frac{1}{2}K_2SO_4}-\lambda_0^{\frac{1}{2}Na_2SO_4}$ etc. Similar results were also obtained with other pairs of salts having either a common anion or a common cation. A few of the results are shown below:

TABLE: λ_0-VALUES FOR PAIRS OF ELECTROLYTES (25°C)

Electrolyte	λ_0	*Difference* $\lambda_{0(1)}-\lambda_{0(2)}$	*Electrolyte*	λ_0	*Difference* $\lambda_{0(1)}-\lambda_{0(2)}$
(1) KCl	149.9		(1) LiCl	115.0	
(2) NaCl	128.8	21.1	(2) $LiNO_3$	110.1	4.9
(1) KNO_3	145.0		(1) KCl	149.9	
(2) $NaNO_3$	123.9	21.1	(2) KNO_3	145.0	4.9
(1) KNO_3	145.0		(1) HCl	426.16	
(2) $LiNO_3$	110.1	34.9	(2) HNO_3	421.3	4.9
(1) $KClO_4$	140.0		(1) NaCl	128.8	
(2) $LiClO_4$	105.08	34.92	(2) $NaNO_3$	123.9	4.9
(1) KCl	149.9				
(2) LiCl	115.0	34.9			

Such a constancy in the difference of λ_0-values of two salts having a common ion is possible only if each ion makes a definite contribution towards the conductivity of the solution irrespective of the value of the other ion. Thus,

$$\lambda_{0(NaCl)} = l_{0Na^+} + l_{0Cl^-} \quad \text{and} \quad \lambda_{0KCl} = l_{0K^+} + l_{0Cl^-}$$

Hence, $\lambda_{0KCl} - \lambda_{0NaCl} = l_{0K^+} - l_{0Na^+}$, whatever salts of sodium and potassium be taken, provided the salts are taken at infinite dilution with common anion.

Kohlrausch therefore proposed that at infinite dilution, each ion makes a definite contribution towards the equivalent conductance of the electrolyte. This contribution is independent of the other ion with which it is present in the solution. The value of the equivalent conductance at infinite dilution (λ_0) of an electrolyte is the sum of contributions of the two ions, such that

$$\lambda_0 = l_c^{\circ} + l_a^{\circ} \qquad \ldots \text{(XX.24)}$$

where l_c° and l_a° are the contributions of the cation and anion repectively, called **'ion conductances'.**

That is, *at infinite dilution, the equivalent conductance is the sum of ion conductances,* which are characteristic of each ionic species. This is commonly known as the *law of independent migration of ions.*

20.14. Determination of Ion Conductances

The individual ionic conductances are usually determined from their transport numbers at infinite dilution. At infinite dilution, an electrolyte is completely dissociated and there is no interionic attraction. In conveying a current, the conduction due to cations would depend upon their charge and their speed. In other words, ion conductance l_c will depend upon charge (n_+z_+e) carried to the cathode and the speed u.

or $\quad l_c^{\circ} = k_1n_+z_+eu$

Similarly for the anions, $\quad l_a^{\circ} = k_1n_-z_-ev$

where n_+, n_- are the numbers of cations and anions with charges z_+e and z_-e each respectively.

∴ From equation (XX.24),

$$\lambda_0 = l_c^{\circ} + l_a^{\circ} = k_1n_+z_+eu + k_1n_-z_-ev = ku + kv$$

or
$$\lambda_0 = k(u + v) \qquad \ldots \text{(XX.25)}$$

where $k = k_1n_+z_+e = k_1n_-z_-e$, the net charges released being equal.

$$\therefore \quad \frac{l_c^{\circ}}{\lambda_0} = \frac{ku}{k(u+v)} = \frac{u}{u+v} \qquad \ldots \text{(XX.26)}$$

and
$$\frac{l_a^{\circ}}{\lambda_0} = \frac{v}{u+v}$$

Using equation (XX. 12,/13), for their transport numbers,

$$\frac{l_c^{\circ}}{\lambda_0} = t_+^{\circ} \quad \text{and} \quad \frac{l_a^{\circ}}{\lambda_0} = t_-^{\circ} \qquad \ldots \text{(XX.27)}$$

or
$$l_c^{\circ} = t_+^{\circ}.\lambda_0 \quad \text{and} \quad l_a^{\circ} = t_-^{\circ}.\lambda_0 \qquad \ldots \text{(XX.28)}$$

The zero-superscripts are used to indicate the state of infinite dilution in the application of these relations.

The transport numbers measured at low concentrations of an electrolyte are extrapolated to zero concentration to obtain t°_+ and t°_-. The knowledge of the transport numbers (t_0) together with a determination of λ_0 would enable us to obtain the values of ion conductances (l°). Some of ion conductance values are incorporated in the Table below:

TABLE: ION CONDUCTANCES AT INFINITE DILUTION (25°C)

Ion	l_c°	*Ion*	l_a°
H^+	349.8	OH^-	198.0
K^+	73.52	Cl^-	76.34
Na^+	50.11	Br^-	78.14
Ag^+	61.9	I^-	76.8
$\frac{1}{2}Ca^{++}$	59.5	NO_3^-	71.46
NH_4^+	73.4	$\frac{1}{2}SO_4^{--}$	80.0
$\frac{1}{2}Mg^{++}$	53.0	Ac^-	40.9

In aqueous solutions, the ionic conductances increase by approximetely 2% per degree centigrade rise in temperature.

Weak Electrolytes: In the case of weak electrolytes, λ_0, the conductance at infinite dilution cannot be directly obtained; the law of independent migration of ions is used for finding out λ_0 for weak electrolytes. To illustrate: λ_0 for acetic acid is evaluated by determining the equivalent conductances of three strong electolytes separately, namely, HCl, NaCl and NaAc. It is easily seen

$$\lambda^\circ_{HCl}+\lambda^\circ_{NaAc}-\lambda^\circ_{NaCl} = (l^\circ_{H+} + l^\circ_{Cl-}) + (l^\circ_{Na+} + l^\circ_{Ac-}) - (l^\circ_{Na+}+l^\circ_{Cl-})$$
$$= l^\circ_{H+} + l^\circ_{Ac-} = \lambda^\circ_{HAc}$$

Since the quantities on the left-hand side are experimentally determined, λ°_{HAc} is known. This method is employed for other weak electrolytes also.

20.15. Ionic Mobilities

The velocity of an ion in a solution depends upon the potential gradient applied. The velocity with which an ion would move under a potential gradient of 1 volt per centimeter in a solution is called its *ionic mobility* or *absolute velocity of the ion.* The limiting value of the ionic mobility is obtained when the solution is at infinite dilution, so that no interionic attraction etc. would arise. The ionic mobilities are related to ion conductances.

We have seen that the ion conductances are

$$l_c^\circ = ku \quad \text{and} \quad l_a^\circ = kv \quad \text{(equation XX.25).}$$

It has been shown that under a potential gradient of 1 volt/cm, the constant k represents the charge carried by 1 gm-equivalent of the ion, *i.e.*, $k = \mathcal{J}$ (one Faraday).

$$\therefore \qquad u = \frac{l_c^\circ}{k} = \frac{l_c^\circ}{\mathcal{J}} \quad \text{and} \quad v = \frac{l_a^\circ}{k} = \frac{l_a^\circ}{\mathcal{J}} \qquad \text{...(XX.29)}$$

The absolute ionic velocity in cm/sec *is obtained by dividing the ionic conductance by* 96500.

TABLE : IONIC MOBILITIES (cm/sec) for SOME COMMON IONS (25°C)

cation	$u \times 10^4$	*anion*	$v \times 10^4$
H^+	36.2	OH^-	20.5
K^+	7.61	SO_4^{--}	8.27
Na^+	5.20	Cl^-	7.90
NH_4^+	7.60	Br^-	8.12
Ag^+	6.40	I^-	7.96
Ca^{++}	6.16	NO_3^-	7.40
Mg^{++}	5.50	Ac^-	4.25

Example 8. Calculate the ionic mobility of the anion in a 0.1 molar solution of NaCl at 25°C. Its transference number is 0.61 and the equivalent conductance at infinite dilution is 127.

We know, $t_a \lambda_0 = l_a^o = v\mathcal{J}$

or $v = \frac{t_a.\lambda_0}{\mathcal{J}} = \frac{0.61 \times 127}{96500} = 7.85 \times 10^{-4}\ \text{cm}^2\ \text{volt}^{-1}\ \text{sec}^{-1}$

Example 9. Given the equivalent conductances of sodium butyrate, sodium chloride and hydrochloric acid as 83, 127 and 426 $\text{ohm}^{-1}\ \text{cm}^2$ at 25°C respectively. Calculate the equivalent conductance of butyric acid at infinite dilution.

$$\lambda^o_{HCl} + \lambda^o_{NaBu} - \lambda^o_{NaCl}$$

$$= l^o_{H+} + l^o_{Cl-} + l^o_{Na+} + l^o_{Bu-} - l^o_{Na+} - l^o_{Cl-}$$

$$= l^o_{H+} + l^o_{Bu-} = \lambda^o_{HBu}$$

$$\therefore 426 + 83 - 127 = \lambda^o_{HBu} \quad i.e., \quad \lambda^o_{HBu} = 382\ \text{ohm}^{-1}\ \text{cm}^2$$

Example 10. At 18°C, the eqv. conductance (λ_0) for HCl and CH_3COONa are 383.5 and 78.4 respectively. The transport numbers of H^+ and Ac^- ions are 0.841 and 0.46 respectively. Calculate the ion conductances of Ac^- and H^+ ions as well as the equivalent conductance of acetic acid at infinite dilution.

Conductance of H^+, $l_{H^+} = t_{H^+}.\lambda^0_{HCl} = 0.841 \times 383.5 = 322.52\ \text{ohm}^{-1}$

Conductance of Ac^-, $l_{Ac^-} = t_{Ac^-}.\lambda^0_{NaAc} = 0.46 \times 78.4 = 36.06\ \text{ohm}^{-1}$

The equivalent conductance of acetic acid (HAc) at infinite dilution,

$$\lambda^o_{HAc} = l_{H^+} + l_{Ac^-} = 322.52 + 36.06 = 358.58\ \text{ohm}^{-1},$$

Example 11. At 18°C, the mobilities of NH_4^+ and ClO_4^- ions are 6.6×10^{-4} and $5.7 \times 10^{-4}\ \text{cm}^2\ \text{volt}^{-1}\ \text{sec}^{-1}$. Calculate equivalent conductance of ammonium chlorate and transport number of the two ions.

We know $\lambda_0 = \mathcal{J}(u + v)$

$$= 96500\,[6.6 \times 10^{-4} + 5.7 \times 10^{-4}] = 118.7\ \text{ohm}^{-1}\ \text{cm}^2$$

The transport number would be

$$t_c = \frac{u}{u+v} = \frac{6.6 \times 10^{-4}}{12.3 \times 10^{-4}} = 0.536; \quad \therefore \quad t_a = 1 - 0.536 = 0.464$$

20.16. Interionic Attraction Theory: Debye-Hückel

The eqv. conductance of an electrolyte depends on the number of ions and their speed. In the case of weak electrolytes, the increase in eqv. conductance with dilution is explained as due to increase in number of ions as the dissociation increases. The speed of ions is not affected, as the ions are few and have no interionic effect.

The strong electrolytes are always completely ionised and hence the number of ions in a given solution would be the same at all concentrations. And yet the eqv. conductance increases with dilution. This is due to the change in the other factor, the ionic speed. At ordinary concentration, the ions are in close proximity and the interionic forces render them unable to move as freely as would otherwise be possible. With dilution, the interionic forces diminish and hence the conductance increases. In 1923, Debye and Hückel proposed a theory known as 'the Debye-Hückel theory of interionic forces' to explain the influence of different forces on a moving ion in an electrolyte. According to this theory, there are three distinct forces which retard the motion of an ion in solution moving under an electric field, *E*. Let us take an ion in solution, say a representative positive ion of charge $+e$, which is called the central ion. The three forces which play on this ion are as follows:

(*i*) Firstly, as the ion moves forward there is a frictional force which retards its motion; this is the viscous force. If the velocity of the ion be u and the medium is assumed to be at rest, then the frictional force,

$$F = -6\pi r\eta u$$

when η = viscosity of the medium, r = radius of the ion.

2. Secondly, in the Debye-Hückel theory it is conceived that each ion is surrounded by an *ionic atmosphere* whose net charge is on the average opposite to that of the central ion. For the positive central ion there would be other ions surrounding it where the net charge would be negative. Similarly a negative central ion would have a positive ionic atmosphere. In the absence of an external applied field, the ionic atmosphere is spherically and symmetrically disposed about the central ion, so that it exerts no net force on the ion (Fig. XX.12a). When an external force is applied such as the potential across two electrodes immersed in solution the ion moves in one direction (say x-axis), but the ionic atmosphere does not have time to adjust itself to remain spherically distributed around the central ion and it lags behind (Fig. XX.12b). As a consequence the ion is retarded in its

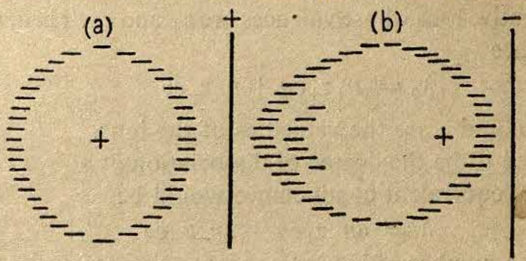


Fig. XX.12

motion by the atmosphere, for the negative charges behind would be greater than those in front of the central ion. This force causing retardation will be in a direction opposite to that of the motion of the central ion. The ionic atmosphere during the motion of the central ion becomes unsymmetrical. This effect on the velocity of an ion is called the *asymmetry effect* or *relaxation effect.*

This opposing force due to the asymmetric ionic atmosphere has been shown to be, $f_2 = -k_1 E\sqrt{C}$ where C is the concentration and k_1, a constant, E = applied potential.

3. Thirdly, under a potential gradient the central ion and the ion atmosphere move in opposite directions. Both the central ion and the atmosphere carry solvent with them. Each of them swim upstream against the oppositely charged solvent pulled along by the other. There is thus a retarding effect called the *electrophoretic effect.* This retarding force is also proportional to $\sqrt{C}$, and is given by

$$f_3 = -k_2 E\sqrt{C}$$

In the steady condition of motion of the ions, the opposing forces would just counterbalance the applied force, Ee.

$$Ee = 6\pi r\eta u + (k_1 + k_2)\sqrt{C}$$

SIMPLE APPLICATIONS OF CONDUCTANCE MEASUREMENTS

20.17. Degrees of Dissociation of Weak Electrolytes

Even in fairly dilute solutions, weak electrolytes are dissociated to a small extent. The number of ions being small, the effect of interionic attraction is negligible for practical purposes. As such the velocities of the ions of weak electrolytes at a definite concentration and at infinite dilution are the same. With dilution, the extent of dissociation increases and hence the number of ions increase. The increase in equivalent conductance is thus due to rise in the degree of dissociation.

Suppose a gm-equivalent of the electrolyte at infinite dilution produces n_+ positive and n_- negative ions whose valences are z_+ and z_-. Then, at infinite dilution, the eqv. conductance

$$\lambda_0 = n_+ z_+ eu + n_- z_- ev \qquad \ldots (a)$$

e = unit charge, u and v are the velocities of the ions.

If α be assumed to be the degree of dissociation at a given concentration (C) of the solution, the equivalent conductance would be

$$\lambda = \alpha n_+ z_+ eu + \alpha n_- z_- ev \qquad \ldots (b)$$

αn_+ and αn_- are the number of ions at concentration (C).

Dividing (b) by (a), $$\alpha = \frac{\lambda}{\lambda_0} \qquad \ldots \text{(XX.30)}$$

Since $\lambda_0 = l_c^\circ + l_a^\circ$, hence $$\alpha = \frac{\lambda}{l_c^\circ + l_a^\circ} \qquad \ldots \text{(XX.31)}$$

This relation is universally employed to find out the degree of dissociation of weak electrolytes.

20.18. Dissociation Constants of Weak Acids

A weak acid solution of HA will have the equilibrium,

$$\begin{array}{ccc} \text{HA} & \rightleftharpoons & \text{H}^+ + \text{A}^- \\ C(1-\alpha) & & \alpha C \quad \alpha C \end{array}$$

C is the concentration and α, the degree of dissociation. Applying the Law of Mass Action, the eqm. constant better known as the dissociation constant of the acid, is given by

$$K_a = \frac{C_{\text{H}^+} \times C_{\text{A}^-}}{C_{\text{HA}}} = \frac{\alpha C \times \alpha C}{(1-\alpha)C} = \frac{\alpha^2 C}{1-\alpha} \qquad \ldots \text{(XX.32)}$$

Now $C = \dfrac{1}{v}$ where v is the volume of the solution, $K_a = \dfrac{\alpha^2}{v(1-\alpha)}$

Again $\alpha = \dfrac{\lambda}{\lambda_0}$, so $K_a = \dfrac{(\lambda/\lambda_0)^2 C}{(1-\lambda/\lambda_0)} = \dfrac{\lambda^2 C}{\lambda_0(\lambda_0 - \lambda)}$ $\qquad \ldots$ (XX.33)

Thus a determination of λ and knowledge of l_c and l_a would enable the evaluation of the dissociation constant.

When the degree of dissociation (α) is very small, we can write the equation (XX.32) approximately as:

$$K_a \approx \alpha^2 C, \quad i.e., \ \alpha = \sqrt{K_a/C} \qquad \ldots \text{(XX.34)}$$

i.e., in the case of very weak electrolytes, the degree of dissociation at a given concentration is proportional to the square root of the dissociation constant.

Example 12. The eqv. conductance of a 0.014 N solution of chloracetic acid is 109.0. The ion conductances of chloracetate and hydrogen ions are 40.2 and 349.8 respectively. Calculate (*a*) the degree of dissociation and (*b*) the dissociation constant of the acid.

(*a*) $\lambda_0 = 349.8 + 40.2 = 390$

$\therefore$ degree of dissociation, $\alpha = \lambda/\lambda_0 = 109/390 = 0.48$

(*b*) The dissociation constant, $K_a = \dfrac{\lambda^2 c}{\lambda_0(\lambda_0 - \lambda)} = \dfrac{(109)^2 \times 0.014}{390(390-109)} = 1.5 \times 10^{-3}$

Example 13. Find out the degree of dissociation and the hydrogen ion concentration at 25°C for a 0.01 molar solution of propionic acid ($K_a = 1.32 \times 10^{-5}$).

Since the acid is a very weak one, we can apply equation (XX.34), *i.e.*,

$$\alpha = (K_a/C)^{\frac{1}{2}} = (1.32 \times 10^{-5}/0.01)^{\frac{1}{2}} = 0.0363.$$

The concentration of hydrogen ions $= 0.01 \times 0.0363 = 3.63 \times 10^{-4}$ gm-eq./litre.

20.19. Degree of Dissociation of Water

Water conducts very feebly, but nevertheless even the purest form of water obtained after repeated careful distillation is slightly dissociated and behaves as a very weak electrolyte. The specific conductance of pure water at 25°C has been found to be 0.58×10^{-7} ohm^{-1} cm^{-1}; its density 0.997/c.c..

Hence, the eqv. conductance of water is $\lambda = \frac{L \times 1000}{C}$

or $\lambda = (0.58 \times 10^{-7}).V_m$, ($V_m$, molar volume)

$$= (0.58 \times 10^{-7}) \times \frac{18}{0.997} = 1.05 \times 10^{-6},$$

Its eqv. conductance on complete dissociation would be

$$\lambda_0 = l_{H^+} + l_{OH^-} = 349.8 + 198 = 547.8$$

∴ The degree of dissociation of water at 25°C

$$\alpha = \frac{\lambda}{\lambda_0} = \frac{1.05 \times 10^{-6}}{547.8} = 1.9 \times 10^{-9}$$

And the conc. of H$^+$ ions, $C_{H^+} = \alpha C = 1.9 \times 10^{-9} \times 1000/18$
$= 1.05 \times 10^{-7}$ gm-equivalents per litre

In pure water the concentrations of H$^+$ and OH$^-$ ions are equal, $C_{H^+} = C_{OH^-}$. The product of the concentrations of the two ions is called **ionic product of water** universally represented as k_w; its value at 25°C,

$$k_w = C_{H^+} \times C_{OH^-} = (1.05 \times 10^{-7})^2 \approx 1 \times 10^{-14} \qquad \ldots \text{(XX.35)}$$

It may be noted that k_w is the *ionic product* of water and not its dissociation constant.

$$H_2O \rightleftharpoons H^+ + OH^-$$

The dissociation constant, $K_{H_2O} = \frac{C_{H^+} \times C_{OH^-}}{C_{H_2O} - C_{H^+}} \approx \frac{C^2{}_{H^+}}{C_{H_2O}}$

$$= \frac{(1.05 \times 10^{-7})^2}{1000/18} = 1.8 \times 10^{-16}$$

20.20. Determination of Solubilities of Sparingly Soluble Salts

The saturated solutions of sparingly soluble salts like $BaSO_4$, AgCl, etc. have extremely low concentrations. These solutions may be regarded as at infinite dilution. If the specific conductance of such a solution be L_s and that of water used for making the solution L_{H_2O}, then the equivalent conductance would be

$$\lambda = (L_S - L_{H_2O}) \frac{1000}{S}$$

where S is the solubility (or conc.) in gm-equivalent of the salt per litre. A correction for conductance of water is introduced here as L_s is quite low.

But here, $\lambda = \lambda_0 = l_e^o + l_a^o$

Therefore, $S = \frac{(L_S - L_{H_2O}) \times 1000}{l_c^o + l_a^o}$ . . . (XX.36)

Example. The specific conductance of $SrSO_4$ in a saturated solution at 25°C is 1.5×10^{-4} and that of water 1.5×10^{-6} ohm^{-1} cm^{-1}, what is the solubility of this salt at 25°C?

Using equation (XX.36)

$$\text{Solubility } S = \frac{(150\times10^{-6}-1.5\times10^{-6})\times1000}{(59.2+79.8)}$$

$\because l_{Sr^{++}} = 59.2$
$l_{SO_4^{--}} = 79.8$
eq. wt. of $SrSO_4 = 92.8$

$= 1.07 \times 10^{-3}$ gm-eqv. per litre
$= 92.8 \times 1.07 \times 10^{-3} = 0.099$ gm/litre.

20.21. Conductometric Titrations

(*i*) **Acid-base titrations.** The strength of an acid or a base can be accurately obtained from conductometric measurements. A known volume of an acid is taken in a conductivity bottle (Fig. XX.13) and its initial conductance is measured. The alkali, whose strength should be much higher than that of the acid (in order to avoid dilution error) is added from a microburette in small amounts and the conductance is measured after each addition. The temperature is maintained constant. The observed conductances are plotted against the volumes of titre added.

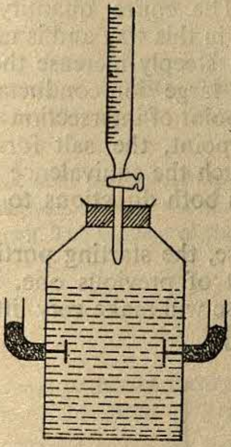


Fig. XX.13. Conductivity bottle for titrations

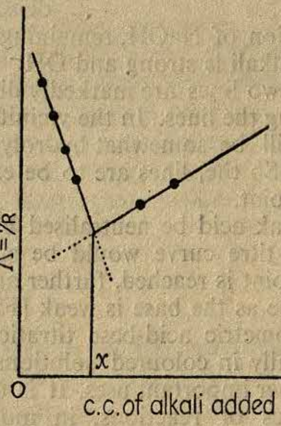


Fig. XX.14. Conductometric titration of strong acid with strong base

(*a*) *Strong acids and strong bases.* Suppose a strong acid (say, HCl) is to be titrated with a strong base (say, NaOH). Since both the acid and the base are strong, these remain completely dissociated. The neutralisation will really mean replacement of H^+ ions by an equal number of Na^+ ions.

$$H^+ + Cl^- \xrightarrow{Na^+ + OH^-} Na^+ + Cl^- + (H_2O)$$

The ionic conductance of H^+ is much higher than that of Na^+. As a result, the conductance of the solution will decrease as more and more NaOH are added. This is shown graphically by the plot of 1/R against volume of titre (Fig. XX.14). In this way when all the H^+ ions are removed, the conductance will reach the lowest limit. Further addition of NaOH means, increase in the numbers of both Na^+ ions and fast moving OH^- ions. These are no longer removed, hence conductance will again increase linearly with addition of titre. The point of intersection of the two lines, *i.e.*, the lowest point, corresponds to minimum conductance which is the exact neutralisation point. Some four or five measurements on either side of the minimum point would give on extension the point of intersection.

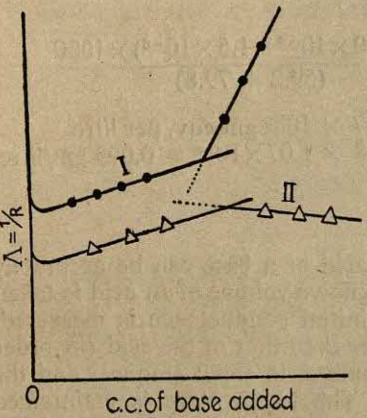


Fig. XX.15. Conductometric titration
I. weak acid by strong base
II. weak acid by weak base

(*b*) *Weak acids and strong bases*. When a weak acid (say, acetic acid) is titrated with a strong base (say, NaOH), the nature of the graph would be somewhat different. Since the acid is weak, the dissociation is poor and hence conductance will be low. As NaOH is added, OH^- ions remove the hydrogen ions. Fresh H^+ ions are produced from the undissociated HAc molecules. Besides, the solution now has some Na^+ ions also. The net result is that there is a rise in the conductivity of the solution. At the starting stage, there may be a little fall in conductivity, due to common ion effect. But later on, this fall will be insignificant compared to the rise in conductivity due to the added new Na^+ ions [Fig. XX.15(1)]. The entire quantity of HAc dissociates slowly in this way and is neutralised. Further addition of NaOH, remaining unused, will steeply increase the conductivity as the alkali is strong and OH^- ions have a large ion-conductance. The slopes of the two lines are markedly different. The point of intersection is obtained by extending the lines. In the vicinity of the end-point, the salt formed from weak acid will be somewhat hydrolysed and as such the equivalence point will not be sharp. So the, lines are to be extended from both directions to reach the equivalence point.

If the weak acid be neutralised by a weak base, the starting portion of the conductance—titre curve would be similar to that of previous one. But when equivalence point is reached, further addition of base will make very little change in conductance as the base is weak [Fig. XX.15 (ii)].

Conductometric acid-base titrations are very useful especially in coloured solutions. Conductometry has other important uses. It is used often in following rates of reactions, in monitoring the flow-process in industries, in vat dyeing, in stream pollution studies, in finding hardness of water, etc.

(*ii*) **Precipitation Reactions.** Reactions in which precipitates are readily formed can also be followed conductometrically. In a reaction of the type,

$$KCl + AgNO_3 \rightarrow KNO_3 + AgCl$$

we have really $K^+ + Cl^- + Ag^+ + NO_3^- \rightarrow K^+ + NO^-_3 + AgCl$. That is, on addition of the titre $AgNO_3$, the K^+ ions remain unchanged in amount, the Cl^- ions are substituted by NO_3^+ ions. The ion conductances of Cl^- and NO_3^- ions are not much different. Hence, the conductance of the solution with successive addition of $AgNO_3$ will not alter much, the line would remain parallel to the axis of precipitant volume, as in Fig. (XX.16). When the equivalence point is passed,

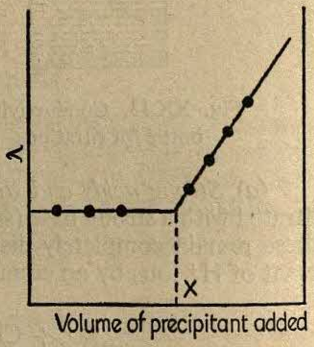


Fig. XX.16. Titration of KCl soln. by $AgNO_3$ soln.

there will be a sharp rise in conductance as unused Ag^+ and NO_3^- are added. The endpoint of the reaction (the point of intersection of the lines) can be determined quite easily.

EXERCISES

I

1. State Faraday's Laws of electrolysis.

Calculate the quantity of caustic soda produced from a Castner cell when 1 kg of chlorine is liberated and the quantity of electricity required. [Ans. 1.127 Kg]

2. What is meant by 'electrochemical equivalent? Show that electrochemical equivalents are proportional to the chemical equivalents.

Calculate the amount of copper deposited by a current of 200 milliamperes in 50 minutes, when $Z_{Cu} = 0.0003296$. [Ans. 0.1978 gm]

3. Define a 'Faraday'. Prove that electrochemical equivalent of hydrogen $Z_{H^+} = 1/F$.

Calculate the quantity of electricity required to reduce 9.84 gm nitrobenzene to aniline. [Ans. 46320 coulomb]

4. A current passes through solutions of (*a*) silver nitrate (*b*) copper sulphate and (*c*) acidulated water. What amounts of copper and silver would be deposited in the time 300 c.c. of hydrogen at N. T. P. collect in (*c*). (Ag = 108, Cu = 63). (Cal. Univ. '37) [Ans. 2.893 gm, 0.844 gm]

5. What is electrolysis? Mention two of its important applications.

The anode of a $CuSO_4$-voltameter is impure copper. A current of 150 amperes were passed through it for 12 hours. How much copper would be deposited on the cathode, if $Z_{Cu} = 0.00033$? [Ans. 2.1 Kg]

6. A current was passed through a KCl solution and a solution of a metallic nitrate. 3.6 gm metal is deposited from the nitrate solution when 4.48 litres of Cl_2 (at N.T.P.) were liberated in the other cell. The sp. heat of the metal is 0.237. What is the formula of the metallic nitrate? [Ans. $M(NO_3)_3$]

II

7. Explain Arrhenius theory of electrolytic dissociation. What are strong and weak electrolytes and in what respects do they differ? How is electrolysis explained from this theory?

8. (*a*) How does the electrolytic dissociation differ from the gaseous dissociation?

(*b*) Sodium added to water bursts into a flame but sodium ions remain in water without any reaction, why?

(*c*) Will a metal present in a salt solution be always deposited on the cathode during electrolysis?

9. What are meant by (*a*) specific conductivity and (*b*) equivalent conductivity of an electrolyte solution? How these two are related?

How would you proceed to determine the equivalent conductivity of a solution? (Cal. Univ. '73).

10. Discuss the effect of dilution on the specific conductivity and the equivalent conductivity of a solution. What is meant by 'equivalent conductivity at infinite dilution'?

How would you obtain the degree of dissociation of a weak electrolyte from conductance measurements?

11. Describe the method of determining the equivalent conductivity of a given solution, What is 'cell constant'?

The sp. conductivity of a N/50 solution of KCl at 25°C is 0.002765 mhos. If the resistance of the same solution in a cell be 2000 ohms, what is the cell-constant? (Kerala Univ. '77)

[Ans. 5.53]

12. 0.5 N solution of a salt surrounding two pt-electrodes 2.1 cm apart and 4.2 sq.cm in area was found to offer a resistance of 25 ohms. Calculate the eqv. conductance of the solution (Osmania Univ. '73) [Ans. 40 mhos]

13. A gm-eqv. of acetic acid in 1000 litres of solution has a specific conductivity of 4.1×10^{-5} ohm^{-1} cm^{-1}. Its equivalent conductivity at infinite dilution is 350 mhos-cm^2. Calculate eqv. conductance and the degree of dissociation of the given solution. (Rangoon Univ.)

[Ans. 41 mho-cm^2; 0.117]

14. (*a*) The sp. conductivity of a 0.5 *N* KCl solution at 20°C is 0.054 ohm^{-1} cm^{-1}. Its equivalent conductivity at infinite dilution is 130.4 ohm^{-1} cm^2. Calculate the degree of dissociation of 0.5*N* KCl solution.

(*b*) At 18°C, the resistance of 0.1*N* KCl in a conductivity cell is 86.8 ohms and that of 0.05*N* NaCl is 203 ohms. What is the equivalent conductivity of 0.05*N* NaCl?

The specific conductance of 0.1*N* KCl at 18°C is 0.011192 mhos.

[Ans. (*a*) 0.828 (*b*) 95.71 mho cm^2]

III

15. What is meant by transport number of an ion? How is it experimentally determined by Hittorf method? ((Mysore Univ.; Kerala Univ. '71)

16. How would you show that during electrolysis the ions move towards the electrodes at different speeds?

Describe the moving boundary method for the determination of transport number of ions.

17. 0.2 molal solution of $CuSO_4$ was electrolysed using copper electrodes. After electrolysis, 36.434 gm solution in cathode chamber contained 0.4415 gm copper. The deposit of silver in the Ag-coulometer in the same circuit was 0.0405 gm. Estimate the transport numbers of copper and sulphate ions. [Ans. $t_{Cu^{++}} = 0.379$]

18. A solution containing 0.2010 gm $AgNO_3$ in 23.8110 gm solution was electrolysed using Ag-electrodes. After electrolysis it was found that 0.2723 gm $AgNO_3$ was present in 23.8823 gm solution in the anode chamber. The Cu-coulometer showed a deposit of 0.0247 gm copper. What is the transport number of Ag^+-ion?

[Ans. 0.461]

19. A silver nitrate solution containing 0.00739 gm of $AgNO_3$ per gm of water is electrolysed between silver electrodes. During the experiment 0.078 gm of Ag was deposited on the cathode. At the end of the experiment anode solution contained 23.14 gm of H_2O and 0.236 gm of $AgNO_3$. What is the transport number of Ag^+? [Ans. $t_{Ag+} = 0.46$]

20. In a moving boundary experiment with a 0.02*N* NaCl solution, a current of 0.0016 ampere moved the boundary through a distance of 6 cm in 2070 seconds. The cross-section of the tube is 0.1115 cm^2. Calculate the transport number of the ions. [Ans. $t_+ = 0.389$]

21. The boundary of a HCl solution (conc. 0.011*N*) with lithium chloride solution moved 7.5 cm in a capillary tube of radius 5 mm. when a current of 11.5 milliamperes were passed for 12 minutes. Calculate the transport number of H^+ ion. [Ans. $t_+ = 0.755$]

22. An aqueous solution of $CuSO_4$ containing 1 gm copper is electrolysed between two copper electrodes till 0.22 gm copper is deposited. After electrolysis, the solution at anode contained 1.165 gm of copper. Calculate transport numbers of Cu^{++} and SO_4^{--} ions. (Punjab Univ. '72)

[Ans. $t_{Cu^{++}} = 0.25$]

IV

24. Explain the terms: (*i*) conductance (*ii*) transport number and absolute velocity of ions. Show how they are related to one another.

The absolute velocity of Ag^+ is 0.00057 cm/sec and of the nitrate ion 0.00069 cm/sec. Assuming complete dissociation, calculate the specific conductivity of $0.01M$ $AgNO_3$ solution. (Osmania Univ. '73) [Ans. 12.16×10^{-4} ohm^{-1} cm^{-1}]

25. State and explain Kohlrausch's Law. Discuss its applications.

At 18°C the eqv. conductances at infinite dilution of NH_4Cl, NaOH and NaCl are 129.8, 217.4 and 108.9 respectively. If the equivalent conductance of a $0.01M$ solution of NH_4OH is 9.33 ohm^{-1} cm^2, calculate the degree of dissociation of NH_4OH at this dilution. (Raj. Univ. '74) [Ans. 0.039]

26. In what units are the following expressed:

(*i*) Sp. conductivity (*ii*) equivalent conductivity (*iii*) ion conductance (*iv*) ionic mobility?

27. The eqv. conductances of NaCl, HCl and monochloracetic acid at 25°C and at infinite dilutions are 127, 426 and 89.8 mho-cm^2. What is λ_0 for monochloracetic acid at 25°C?

[Ans. 388.8 mho–cm^2]

28. The eqv. conductance of an infinitely dilute solution of NH_4Cl is 150 and the ion conductances of OH^- and Cl^- ions are 198 and 76 $ohm^{-1}cm^2$. What will be the value of λ_0 for NH_4OH? If the eqv. conductance of $0.01N$ NH_4OH solution be 9.6, what will be its degree of dissociation?

[Ans. $\lambda_0 = 272$ ohm^{-1} cm^2, $\alpha = 3.53\%$]

29. The resistance of a conductivity cell filled with $0.02N$ KCl at 18°C is 17.6 ohms; filled with $0.1N$ acetic acid resistance is 92 ohms. The specific conductance of $0.02N$ KCl at 18°C is 0.0024 $ohm^{-1}cm^{-1}$. At 18°C, $l_{H^+} = 315$, $l_{Ac^-} = 35$. Show that $0.1N$ acetic acid is dissociated to an extent of 1.31% at 18°C.

30. At 25°C, the mobility at infinite dilution of NH_4^+ ion is 76×10^{-5} and that of acetate ion is 42×10^{-5} cm^2 $volt^{-1}$ sec^{-1}. Calculate λ_0 for ammonium acetate and the transport numbers of the two ions. [Ans. $\lambda_0 = 113.9, t_+ = 0.644$]

31. What is the ionisation constant of chloracetic acid if the eqv. conductance of its $0.014N$ solution be 109 at 25°C. Given $l_{H^+} = 349.8$, $l_{A^-} = 40.2$. [Ans. $k_{a'} = 1.09 \times 10^{-3}$]

32. The Arhenius dissociation constant of propionic acid is 1.35×10^{-5}. Calculate the degree of dissociation and the conc of H^+ ions in a 0.005 molar solution.

[Ans. $C_{H^+} = 2.6 \times 10^{-4}$; $\alpha = 5.19 \times 10^{-2}$]

33. The specific conductance of sat. solution of TlBr is 2.16×10^{-4} and that of water 0.04×10^{-6}. The eqv. conductance at infinite dilution is 138.2. Find out the solubility of thallous bromide in gm per litre at the same temperature. [Ans. 0.4435 gm/litre]

34. The sp. conductance of a saturated solution of AgCl is 1.55×10^{-6} ohm^{-1} cm^{-1} and that of water 4.3×10^{-7} ohm^{-1} cm^{-1}. In a field of 1 volt per cm, the mobilities of chloride and silver ions are 5.6×10^{-4} and 6.8×10^{-4} cm/sec. Calculate the solubility product of AgCl. The temperature is always the same. [Ans. 8.5×10^{-11}]

CHAPTER 21

ELECTROCHEMICAL CELLS

21.1. Galvanic Cells

In a voltameter or *electrolytic cell,* we have seen, electric energy is used to perform a chemical change. On the other hand, a *galvanic cell* is a device in which the free energy of a chemical process is converted into electrical energy. These cells are rightly called *electrochemical cells.*

Usually such a cell consists of two electrodes partially immersed in suitable electrolytes. When the electrodes are externally connected by a metallic wire, a current flows through the wire and chemical changes occur inside the cell.

Reversible and Irreversible Cells. The electrochemical cells may be reversible or irreversible. In a reversible cell the chemical reaction occurring in the cell may proceed in either direction depending upon the direction of flow of the current. When the circuit of a cell is closed, a reaction occurs in the cell and a current is obtained. Thereafter, if we apply a driving force from an external em.f. so as to cause a current to flow in the opposite direction, the chemical action is exactly and fully reversed. Both the processes must be carried out very slowly. When these requirements are satisfied, the cell is *reversible.* When the chemical process cannot be exactly reversed by the application of external e.m.f., the cell is *irreversible.* To illustrate a reversible galvanic cell, we may cite the familiar Daniell cell.

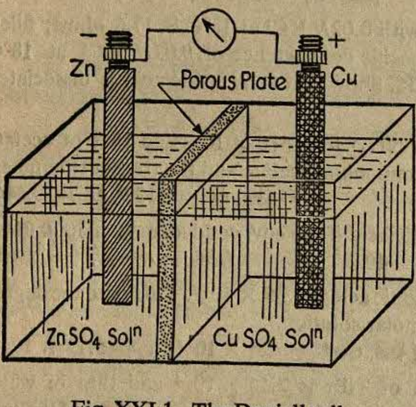


Fig. XXI.1. The Daniell cell

In a Daniell cell, a zinc rod partially immersed in $ZnSO_4$ solution and a copper rod in $CuSO_4$ solution are the two electrodes. The two solutions are separated by a porous barrier which allows the current to pass through but prevents mass diffusion (Fig. XXI.1).

An equilibrium exists between the atoms in the electrode and the ions in solution at each electrode;

$$Zn \rightleftharpoons Zn^{++} + 2e \qquad Cu \rightleftharpoons Cu^{++} + 2e$$

During the production of current, zinc atoms pass into solution as Zn^{++} ions leaving behind two electrons each in the metal electrode. On the other hand, copper ions from the solution are deposited on the copper electrode by accepting two electrons each from the metal. So, there is an excess of electrons in the zinc electrode and dearth of the same at the copper electrode. When the circuit is closed, the electrons from zinc flow to copper through the wire to feed the copper ions in the process of discharge of the latter. This is how the current (and thus electric energy) is produced.

The zinc electrode, where zinc gives up its electrons, *i.e.*, oxidation occurs, is the negative electrode of the cell. The copper electrode, where copper ions take up electrons, *i.e.*, reduction occurs, is the the positive electrode. The galvanic cell is represented as,

$$\text{Zn} \mid \text{Zn}^{++} (\text{conc. } c_1) \parallel \text{Cu}^{++} (\text{conc. } c_2) \mid \text{Cu}$$

where vertical lines indicate phase boundaries.

The cell reaction is $\text{Zn} + \text{Cu}^{++} = \text{Zn}^{++} + \text{Cu}$

It is usual to write the negative electrode of the cell (Zn) on the left and the positive (Cu) on the right in representing the cell. It is the common convention that the current in the *external circuit* is considered to flow from the + ve to the −ve (Cu to Zn), although the electrons are flowing through the wire in the opposite direction.

When $2\triangle q$ coulombs of electricity are produced by slowly extracting it from the Daniell cell, $\triangle q \times 65/96500$ gm Zn dissolves at the −ve electrode and $\triangle q \times 63.5/96500$ gm Cu is deposited at the + ve electrode. If now an external e.m.f. slightly higher than the cell e.m.f. be applied such that $2\triangle q$ coulombs of electricity pass in the opposite direction, the cell returns to its original state; *i.e.*, the zinc dissolved earlier would be deposited on the zinc electrode and the copper deposited previously would redissolve from the copper electrode. The cell is thus reversible.

Many reversible electrochemical cells are in use, such as,

Cell	*Chemical reaction*
(*i*) $\overset{-}{\text{Zn}} \mid \text{Zn}^{++}(\text{soln}) \mid \text{Hg}_2^{++}(\text{soln}) \mid \overset{+}{\text{Hg}}$;	$\text{Zn} + \text{Hg}_2^{++} = \text{Zn}^{++} + 2\text{Hg}$
(*ii*) $\overset{-}{\text{Pb}} \mid \text{H}_2\text{SO}_4 \mid \overset{+}{\text{PbO}_2(\text{Pb})}$;	$\text{PbO}_2 + \text{Pb} + 2\text{H}_2\text{SO}_4 = 2\text{PbSO}_4 + 2\text{H}_2\text{O}$

On the other hand, if we consider the cell

$$\text{Zn} \mid \text{H}_2\text{SO}_4 \mid \text{Cu}$$

In which 1 faraday of electricity is produced, when 1 gm-equivalent zinc goes into solution and one gm-equivalent hydrogen is liberated at the cathode (Cu). If now 1 faraday of electricity is passed through the cell in the opposite direction 1 gm-equivalent of copper goes into solution and 1 gm-equivalent of hydrogen is liberated at the zinc-electrode. The original state is not reproduced; the reaction is also not reversed. This is an *irreversible* cell.

The origin of the e.m.f. of a cell is explained as follows. A metal is regarded as an assembly of metal ions and free electrons. When the metal is in contact with water, the metal ions have a tendency to enter into the liquid. This tendency was called '*electrolytic solution tension*' by Nernst. When some metal ions leave the solid, the solid becomes negatively charged due to excess electrons and the solution is positively charged. Due to electrostatic force any further transference of the metal is prevented and the ions attracted by the negatively charged metal remain very near to the metal surface forming a double layer. If the metal is placed in a solution of its own ions, the metals ions as before tend to pass into solution while the metal ions present in solution in virtue of its osmotic pressure would attempt to enter into the solid metal. The difference in the rates of these two opposing processes leads to the development of a potential difference at the electrode. If the rate of transfer of metal ions into solution be greater, there will be excess of electrons in the metal rendering it to be negative which will attract positive ions forming a double layer. If, on the other hand, the rate of discharge of metal ions on the solid be greater than the rate of the dissolution of ions from the metal, then the metal will be positive and it will attract negative anions forming a double layer. In any case a double layer is formed giving rise to electrical potential difference (Fig XXI. 2) which is called the electrode potential. An arbitrary assumption regarding disposition of charges on the electrode surfaces has been made. To wit: In the Daniell cell, the zinc electrode is negative (more zinc ions pass into solution), there is excess of electrons in zinc electrode. The copper electrode is positive (more copper ions enter into the metal) and there is paucity of electrons. Hence when the two electrodes are externally connected, the electrons spontaneous flow from high concentration (in zinc) to low concentration (in copper) and we obtain the flow of current or electricity.

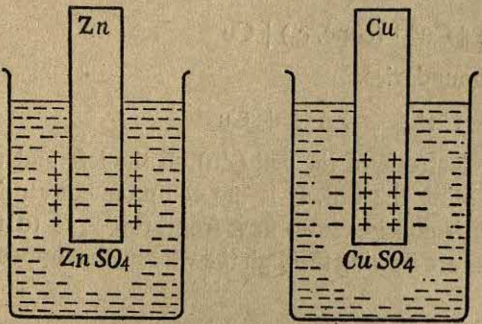


Fig. XXI.2. Double layers

The e.m.f. of the cell is the algebraic sum of the two electrode potentials of the cell.

21.2. Measurement of EMF of Cells

The e.m.f. of a cell is measured with the help of a potentiometer. The principle involved can be easily understood from Fig. XXI.3. AB is the potentiometer slide wire of uniform cross-section and having high resistance. A storage cell C is connected across the terminals of the slide wire *AB*, such that potential drops from A to B. Now the cell X, whose e.m.f. is required, is connected to A, so that its e.m.f. opposes that of C. (That is, A is connected to positive terminals of both X and C.) The other terminal of cell X is connected through a galvanometer (G) to a sliding contact P. This is moved along the slide wire until there is no deflection in the galvanometer. This means that the e.m.f. of the cell X just balances the drop of potential between A and P. of known e.m.f.

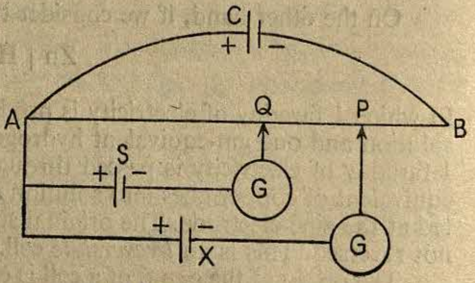


Fig. XXI.3. Measurement of EMF of a cell

Next a standard cell (S) of known e.m.f. is taken to replace the cell X and the experiment is repeated. The e.m.f. of the cell S now opposes that of C in the slide wire. Let the contact point now be Q when there would not be any deflection in the galvanometer. That means the drop of potential in the slide wire from A to Q just balances the e.m.f. of the standard cell.

If E_x and E_s be the e.m.f. of the given cell and the standard cell, then

$$\frac{E_x}{E_s}=\frac{\text{Drop of potential from A to P}}{\text{Drop of potential from A } to \text{ Q}}=\frac{\text{Resistance of AP}}{\text{Resistance of AQ}}=\frac{\text{length AP}}{\text{length AQ}}$$

since the wire is of uniform cross section. The two lengths being known and since E_s, the e.m.f. of the standard cell is known, E_x is easily determined.

The most widely used standard is the *Weston Cell*, which is composed as

$$\begin{array}{c|c|c|c|c} \text{Cd(Hg)}_x & \text{CdSO}_4,\ 8/3\text{H}_2\text{O} & \text{CdSO}_4 & \text{Hg}_2\text{SO}_4 & \text{Hg;} \\ [12.5\%\ \text{Cd amalgam} & (s) & \text{(sat. soln)} & \text{(solid)} & \end{array}$$

in which the cell reaction is

$$Cd + Hg_2SO_4 = CdSO_4 + 2Hg$$

The cell is prepared in a H-shaped vessel—one arm containing the electrode 12.5% Cd-amalgam and the other arm containing mercury in contact with a paste of Hg and mercurous sulphate. The whole of the vessel is then filled up with saturated solution of $CdSO_4$. Some crystals of $3CdSO_4$, $8H_2O$ being added over the negative electrode. The vessel is then sealed. The electrodes are connected to the external circuit through two Pt-wires sealed at the bottom of the two electrodes (Fig. XXI.4).

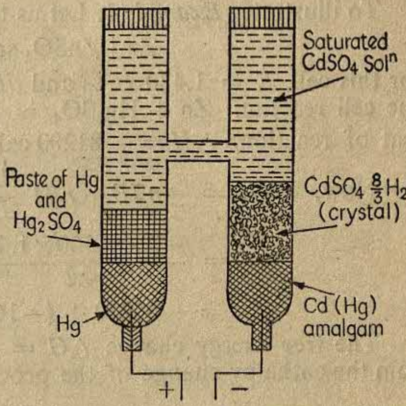


Fig. XXI.4. A standard cell (Weston Cell)

Its emf is measured by comparison with p.d. across a standard known resistance carrying an absolutely known current (say, Ag-coulometer).

The e.m.f. of Weston cell remains constant for a long period and has a high reproducibility. Its temperature coefficient is also quite small. At 20°C,

$$E = 1.01845 \text{ volts and } \frac{dE}{dt} = -0.00004 \text{ volts degree}^{-1}$$

21.3. EMF of a Cell and Free Energy Change

If E be the emf of the cell supplying a quantity of electricity Q, then the electrical energy is EQ. With each equivalent of reactant involved is associated one Faraday, ($\mathcal{J}$) of electricity. If n equivalents of reaction occurs,

$$\text{electrical energy produced} = n\mathcal{J}E$$

It was Helmholtz who first pointed out that in a reversible cell *the decrease in the free energy of the process is equal to the electrical energy obtained from a galvanic cell.* That is,

$$-\triangle G = n\mathcal{J}E \qquad \ldots\text{(XX.1)}$$

From the Gibb's Helmholtz relation,

$$\triangle G = \triangle H + T\left[\frac{\partial(\triangle G)}{\partial T}\right]_P$$

Hence $$-n\mathcal{J}E = \triangle H + T\left[\frac{\partial(-n\mathcal{J}E)}{\partial T}\right]_P$$

or $$E = \frac{-\triangle H}{n\mathcal{J}} + T\left(\frac{\partial E}{\partial T}\right)_P \qquad \ldots\text{(XXI.2)}$$

This relation is universally used to evaluate the e.m.f. of a cell.

It is further known from Thermodynamics that

$$\triangle S = -\left[\frac{\partial(\triangle G)}{\partial T}\right]_P$$

$$\therefore \qquad \triangle S = -\left[\frac{\partial(-nJE)}{\partial T}\right]_P = nJ\frac{dE}{dT} \qquad \ldots (\text{XXI.3})$$

We can thus measure the entropy-change from the temperature-coefficient of the e.m.f. of a cell. Hence, the knowledge of the e.m.f. of a cell permits the evaluation of $\triangle S$, $\triangle G$ and also $\triangle H$ of a chemical process (since $\triangle H = \triangle G + T\triangle S$).

To illustrate: *Example* 1. Let us take the Clarke cell,

$$\text{Zn} \mid \text{ZnSO}_4 \text{ solution} \parallel \text{Hg}_2\text{SO}_4 \mid \text{Hg}$$

For this cell, $E = 1.420$ volts and $dE/dT = -1.2 \times 10^{-3}$ volts/°C, at 25°C.
The cell reaction: $Zn + Hg_2SO_4 = ZnSO_4 + 2Hg$;
heat of reaction, $\triangle H = -81200$ cal

$$\text{Now,} \quad \triangle H = -nJE + nJT\frac{dE}{dT}$$

$$= \frac{-2\times96500\times1.420}{4.2} + \frac{2\times96500}{4.2} \times (273+25)\times(-1.2\times10^{-3})$$

$$= -65250 + (-16710) = -81960 \text{ cal}$$

The free energy change $\triangle G = -nJE = -65250$ cal. It is thus different from the enthalpy-change of the process, which is $\triangle H = -81960$.

20.4. EMF of Cells and Equilibrium Constant (Nernst Equation)

If the chemical change in the galvanic cell is represented by

$$A + B \rightleftharpoons C + D$$

then the free energy change ($\triangle G$) of the process would be

$$\triangle G = -RT\ ln\ K_c + RT\Sigma\nu\ ln\ C \qquad \ldots (\text{XXI.4})$$

where K_c is the eqm. constant. For greater accuracy, activities should be used in place of concentrations (C).

If all the participants be taken in the standard state, *i.e.* at unit concentration ($C = 1$), then the standard free energy ($\triangle G^\circ$) will be

$$\triangle G^\circ = -RT\ ln\ K_c \qquad \ldots (\text{XXI.5})$$

We have seen $\triangle G = -nJE$, and $\triangle G^\circ = -nJE^\circ$ ... (XXI.6)

where E is the emf of the cell in the given state and E° is the standard emf of the cell. Substituting (XXI.6) in equations (XXI.4 and 5), we have, $nJE^\circ = RT\ ln\ K_c$ ... (XXI.6a)

$$\text{and} \qquad -nJE = -nJE^\circ + RT\ \Sigma\nu\ ln\ C$$

$$\text{or} \qquad E = E^\circ - \frac{RT}{nF}\Sigma\nu\ ln\ C = E^\circ - \frac{2.303RT}{nJ}\ \Sigma\nu \log C \qquad \ldots (\text{XXI.7})$$

At 25°C, the value of 2.303 RT/J is 0.0591. So, at 25°C,

$$E = E^\circ - \frac{0.0591}{n}\Sigma\nu \log C \qquad \ldots (\text{XXI.8})$$

These are the Nernst equations for galvanic cells. These equations enable the evaluation of the eqm. constant from emf measurements and *vice versa.*

Example 2. At 25°C, the standard e.m.f. of the Daniell cell is 1.1 volts. Calculate K_c. The reaction is

$$Zn + Cu^{++} \rightarrow Cu + Zn^{++}$$

$$K_c = \frac{C_{cu} \times C_{zn}{}^{++}}{C_{cu}{}^{++} \times C_{zn}} = \frac{C_{zn}{}^{++}}{C_{cu}{}^{++}} \quad (\text{since } C_{cu} = C_{zn} = 1)$$

$$\therefore \quad E^\circ = \frac{0.0591}{n} \log K_c$$

$$\text{or} \quad 1.1 = \frac{0.0591}{2} \log K_c, \text{ or } K_c = 1.7 \times 10^{37}$$

Example 3. At 25°C, the eqm. constant for the reaction

$$AgClO_4 + Fe\,(ClO_4)_2 \rightleftharpoons Ag + Fe\,(ClO_4)_3$$

was found to be 2.00. what would be standard emf of the cell based on this reaction.

The cell is: $Fe^{++}-Fe^{+++}\,(Pt)\,\|\,Ag^+\,|\,Ag$.

$$E^\circ = \frac{0.0591}{1} \log 2 = 0.018 \text{ volt.}$$

201.5. Single Electrodes

An electrochemical cell must have two electrodes, positive and negative. Each of these two is known as a **Half-cell** or a **Single electrode.** At each electrode, there would occur transfer of electrons from the electrolyte to the electrode or *vice versa* when the current flows. Different types of electrodes are in use, some of which are mentioned here.

(*a*) **Metal-Metal ion electrodes:** In this type a metal is in equilibrium with a solution of its ions, such as zinc in zinc sulphate solution, silver in silver nitrate solution, etc. The electrode processes may be represented as,

Electrode process	electrode
$Ag \rightleftharpoons Ag^+ + \epsilon$	Ag/Ag^+
$Cu \rightleftharpoons Cu^{++} + 2\epsilon$	Cu/Cu^{++}
$H \rightleftharpoons H^+ + \epsilon$	H/H^+
$Cl^- \rightleftharpoons Cl + \epsilon$	Cl^-/Cl

In some cases of metal-metal ion electrodes, such as those of potassium, sodium, calcium, etc. the pure metals are too active to use them in aqueous solution of their ions. As such these are used in the form of their mercury amalgams, hence called *amalgam electrodes,* represented as:

$Pb(Hg) \rightleftharpoons Pb^{++} + 2\epsilon$	$Pb(Hg)/Pb^{++}$
$K\,(Hg) \rightleftharpoons K^+ + \epsilon$	$K(Hg)/K^+$ etc.

(*b*) **Gas electrodes:** In the case of non-metal electrodes which are often non-conductors and sometimes gaseous, a special arrangement is needed for conduction. Usually a platinum foil or wire coated with plainum black is kept immersed in the solution and the non-metal gas is bubbled about it so that the Pt-black is fully saturated with adsorbed gas. The adsorbed molecules and their ions in solutions are thus brought in contact through the platinum. The Pt-black serves to establish equilibrium between the gas and its ions in solution and facilitates electric contact. The electrodes are represented as

$$H_2(Pt) \mid H^+ \qquad\qquad Cl^- \mid Cl\,(Pt\text{-}Ir)$$

(*c*) **Metal-Sparingly soluble salts electrodes:** A metal with one of its sparingly soluble salts in contact with a solution having the same anion may also form a good electrode, *e.g.*,

$$\begin{aligned}&Ag \mid AgCl(s),\ KCl\ \text{soln}\\&Hg \mid Hg_2Cl_2(s),\ KCl\ \text{soln}\\&Pb \mid PbSO_4(s),\ K_2SO_4\ \text{soln. etc}\end{aligned}$$

The elctrode process is as follows. Consider the silver-silver chloride electrode. There are some silver ions in the solution though very small in view of low solubility of silver chloride. Now some silver ions will pass into solution as $Ag \rightleftharpoons Ag^+ + \epsilon$. Since the solution is saturated with AgCl, the silver ions produced will combine with Cl^- ions to restore solubility equilibrium, $Ag^+ + Cl^- \rightleftharpoons AgCl(s)$. The net result is the removal of chloride ion from solution with electrons transferred to the metal.

$$\begin{aligned}Ag(s) &\rightleftharpoons Ag^+ + \epsilon\\Ag^+ + Cl^- &\rightleftharpoons AgCl\,(s)\\\hline Ag(s) + Cl^- &\rightleftharpoons AgCl(s) + \epsilon\end{aligned}$$

The electrode therefore is really reversible with respect to the anion *i.e.*, Cl^- ion.

(*d*) **Oxidation-Reduction electrodes:** An inert metal, such as platinum, immersed in a solution containing a mixture of the oxidised and the reduced states of a system, constitutes an important type of an electrode.

Thus, a Pt-wire dipped in a mixture of the solutions of Fe^{++} and Fe^{+++} salts, or Sn^{++} and Sn^{++++} salts, etc. will serve as a single electrode. The reactions in such a case involve transfer of electrons between the oxidised and the reduced forms, *e.g.*,

$$\begin{aligned}&Fe^{++} = Fe^{+++} + \epsilon\\&Sn^{++} \rightleftharpoons Sn^{++++} + 2\epsilon\\&Mn^{++} + 4H_2O \rightleftharpoons MnO_4^- + 8H^+ + 5\epsilon\\&\underset{\text{Hydroquinone}}{C_6H_4(OH)_2} \rightleftharpoons \underset{\text{Quinone}}{C_6H_4O_2} + 2H^+ + 2\epsilon,\ \text{etc.}\end{aligned}$$

Oxidation, in modern terminology, means giving up of electrons. Thus ferrous ion is oxidised to ferric ion and zinc atom is oxidised to Zn^{++} ion, Cl^- ion is oxidised to chlorine atom. Reduction is the opposite process and it involves the acceptance or taking up of electrons, as Cu^{++} ions are reduced to Cu atoms.

Oxidation	*Reduction*
$Fe^{++} \rightarrow Fe^{+++} + \epsilon$	$Cu^{++} + 2\epsilon \rightarrow Cu$
$Zn \rightarrow Zn^{++} + 2\epsilon$	$Hg^{++} + \epsilon \rightarrow Hg^{+}$; etc.
$Cl^{-} \rightarrow Cl + \epsilon$	

Thus, Fe^{+++}, Zn^{++}, Cu^{++}, Cl, Hg^{++}, etc. are the oxidised states called *oxidants*, and Fe^{++}, Zn, Cu, Cl^{-}, Hg^{+}, etc. are the reduced states, called *reductants*.

A reversible electrode therefore will involve an oxidant and a reductant. The different processes in the electrodes may be represented as:

Electrode Process	*Oxidant*	*Reductant*
$Zn \rightleftharpoons {}^{++} + 2\epsilon$	Zn^{++}	Zn
$Ag + Cl^{-} \rightleftharpoons AgCl + \epsilon$	AgCl	Cl^{-}
$Fe^{++} \rightleftharpoons Fe^{+++} + \epsilon$	Fe^{+++}	Fe^{++}

Hence, in any electrode, the process involved may be expressed as:

$$\text{Reductant} \rightleftharpoons \text{Oxidant} + n\epsilon$$

In a Daniell cell, oxidation occurs at the zinc electrode which is negative and reduction occurs at the copper electrode which is positive.

$$Zn \rightarrow Zn^{++} + 2\epsilon \qquad Cu^{++} + 2\epsilon \rightarrow Cu$$

Likewise in all cells the electrode where oxidation occurs is the negative electrode and the electrode where reduction occurs is the positive electrode.

21.6. Electrode Potentials

At each electrode, there is a double layer with positive and negative charges facing one another (Fig. XXI.2) and a potential develops. This is called the 'electrode potential'. Nernst equation is employed to evaluate such electrode potentials.

(*a*) Let us consider the zinc electrode dipped in a solution of Zn^{++} ions. Let the actual process occurring there be one of oxidation.

Electrode: $Zn \mid Zn^{++}$; Process: $Zn \rightarrow Zn^{++} + 2\epsilon$

If ξ_{Zn} and ξ^{o}_{Zn} denote the electrode potentials of zinc in a solution of Zn^{++} ions of concentration $C_{Zn^{++}}$ and in a solution of unit concentration respectively, then applying Nernst equation (XXI.7).

$$\xi_{Zn} = \xi^{o}_{Zn} - \frac{RT}{2J} \ln \frac{C_{Zn^{++}}}{C_{Zn}} = \xi^{o}_{Zn} - \frac{RT}{2J} \ln \frac{C_{\text{oxidant}}}{C_{\text{reductant}}}.$$

Since $C_{Zn} = 1$, we have $\xi_{Zn} = \xi^{o}_{Zn} - \frac{RT}{2J} \ln C_{Zn^{++}}$ ... (XXI.9)

ξ^{o}_{Zn} is the electrode potential of zinc in the standard solution of Zn^{++} ions of unit concentration. ξ^{o}_{Zn} is called the *standard electrode potential* of zinc. Further, it has been assumed that oxidation has occurred at this electrode, so ξ^{o}_{Zn} is the *standard oxidation potential* of zinc.

If instead of oxidation, reduction occurs at this electrode, the process would be $Zn^{++} + 2\epsilon \rightarrow Zn$, for example in the cell: $K(Hg) \mid K^+ \parallel Zn^{++} \mid Zn$ in which Zn is the positive electrode.

The electrode potential of zinc electrode will be its *reduction potential.* For a given electrode the oxidation and reduction potentials are exactly equal in magnitude but opposite in sign.

For example:

Electrode	*activity*	*oxn. potential*	*redn. potential*
Zn	0.1	+ 0.792	−0.792 (volts)
Cu	1.0	−0.337	+ 0.337 (volts)

To generalise, the potential of an electrode where oxidation occurs is expressed as

$$\xi_M = \xi^o_M - \frac{RT}{nJ} \ln \frac{C_{oxidant}}{C_{reductant}} \qquad \ldots (XXI.10)$$

For accurate values, concentrations should be replaced by activities.

(*b*) *Gas Electrodes: Chlorine electrode*

Electrode: $Cl_2(Pt)—Cl^-$; *Process:* $Cl^- \rightarrow \frac{1}{2}Cl_2 + \epsilon$

The electrode potential would be

$$\xi_{Cl_2} = \xi^o_{Cl_2} - \frac{RT}{J} \ln \frac{C^{\frac{1}{2}}_{Cl_2}}{C_{Cl^-}} = \xi^o_{Cl_2} - \frac{RT}{J} \ln \frac{C_{oxidant}}{C_{reductant}} \qquad \ldots (XXI.11)$$

The expression is the same as in eqn. XXI.10.

(*c*) *Metal-Insoluble salts electrode: Calomel electrode*

Electrode: $Hg—Hg_2Cl_2(s) \mid Cl^-$; *Process:* $2Hg + 2Cl^- = Hg_2Cl_2 + 2\epsilon$

The electrode potential would be

$$\xi_{Cal} = \xi^o_{Cal} - \frac{RT}{2J} \ln \frac{C_{Hg_2Cl_2(s)}}{C_{Hg} \cdot C^2_{Cl^-}}$$

$$= \xi^o_{Cal} + \frac{RT}{J} \ln C_{Cl^-} \quad (\text{since } n = 2) \qquad \ldots (XXI.12)$$

(*d*) *Oxidation-Reduction Electrodes or Redox Electrodes: Ferrous-ferric electrode*

Electrode: $(Pt) \mid Fe^{++}, Fe^{+++}$; *Process:* $Fe^{++} \rightarrow Fe^{+++} + \epsilon$

From eqn (XXI.7), $\xi_{redox} = \xi^o_{redox} - \dfrac{RT}{J} \ln \dfrac{C_{Fe^{+++}}}{C_{Fe^{++}}}$

$$= \xi^o_{redox} - \frac{RT}{J} \ln \frac{C_{oxidant}}{C_{reductant}} \qquad \ldots (XXI.13)$$

ξ^o_{redox} is the standard oxidation potential of the redox electrode when both the reduced and the oxidised forms are at unit concentrations.

For all types of electrodes, the oxidation potential (ξ) is given by

$$\xi = \xi^0 - \frac{RT}{J} \ln \frac{C_{\text{oxidant}}}{C_{\text{reductant}}}$$

The electrode potential depends upon the temperature and the concentration of the cells.

21.7. EMF of Cells and Electrode Potentials

The emf of the galvanic cells can be computed from the electrode potentials. The principle is

The emf of a cell is the algebraic sum of its electrode potentials.

In every cell oxidation occurs at the negative electrode and reduction at the positive electrode. To compute the emf of the cell, take the sum of the *oxidation potential* of the negative electrode and the *reduction potential* of the positive electrode. It is to be remembered that the reduction potential of an electrode is the same as its oxidation potential with the sign changed.

The emf of the cell, $E = \xi^{ox^n}_{anode} + \xi^{red}_{cathode} = \xi^{ox^n}_{anode} - \xi^{ox^n}_{cathode}$ . . . (XXI.14)

Take the Daniell cell, $Zn + Cu^{++} \rightarrow Cu + Zn^{++}$, in which zinc is the negative and copper is the positive electrode.

From the Nernst equation XXI.7, the emf of the cell is

$$E = E^\circ - \frac{RT}{nJ} \ln \frac{C_{Zn^{++}} C_{Cu}}{C_{Cu^{++}} C_{Zn}} = E^\circ - \frac{RT}{nJ} \ln \frac{C_{Zn^{++}}}{C_{Cu^{++}}} \qquad \ldots (A)$$

Again, following eqn XXI.9, the oxidation potentials of Zn and copper electrodes are

$$\xi^{ox^n}_{Zn} = \xi^0_{Zn} - \frac{RT}{nJ} \ln C_{Zn^{++}}$$

$$\xi^{ox^n}_{Cu} = \xi^0_{Cu} - \frac{RT}{nJ} \ln C_{Cu^{++}}$$

From eqn (XXI.14) the emf of the cell would be

$$E = \xi^0_{Zn} - \frac{RT}{nJ} \ln C_{Zn^{++}} - \left(\xi^0_{Cu} - \frac{RT}{nJ} \ln C_{Cu^{++}}\right)$$

$$= (\xi^0_{Zn} - \xi^0_{Cu}) - \frac{RT}{nJ} \ln \frac{C_{Zn^{++}}}{C_{Cu^{++}}}$$

$$= E^0 - \frac{RT}{nJ} \ln \frac{C_{Zn^{++}}}{C_{Cu^{++}}}$$

It is the same as in (A) above. The (normal) standard emf of the cell is the algebraic sum of the standard electrode potentials, $E^\circ = \xi^0_{Zn} - \xi^0_{Cu}$. The emf of the cell can thus be computed from the electrode potentials.

21.8. Standard Electrode Potentials

In order to assign numerical values to the electrode potentials, it is necessary, to choose a standard electrode and assign an arbitrary value to the potential of the same. For this purpose the reference electrode is the *normal hydrogen electrode.* $\underset{(1\ \text{atm})}{H_2(Pt)_{gas}}|H^{+}_{(a=1)}$, in which pure hydrogen gas at unit pressure is kept in contact with solution containing H^+-ion of unit activity through adsorption on Pt-black by continuous bubbling of the gas. A common laboratory arrangement of H_2-electrode is shown in Fig. XXI.5. *The potential of this normal hydrogen electrode is taken as zero at all temperatures.* It should be emphasised that if the acid solution has H^+ ion activity other than unity the electrode potential would no longer be zero. For

$$\xi_{H_2} = \xi^0_{H_2} - \frac{RT}{nJ} \ln a_{H^+} = -\frac{RT}{nJ} \ln a_{H^+}$$

$$\text{if } a_{H^+} \neq 1;\ \xi_{H_2} \neq 0.$$

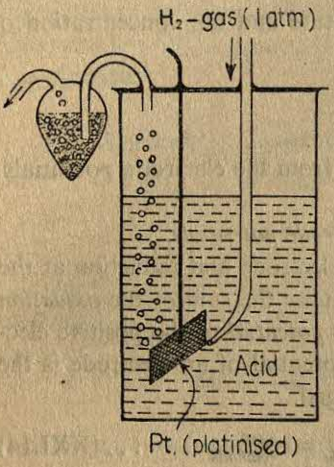


Fig. XXI.5. H_2-Electrode

The potentials of other electrodes are expressed in reference to the normal hydrogen electrode. To evaluate the potential of any other single electrode, it is necessary to couple it with a standard or normal hydrogen electrode and the emf of the galvanic cell is measured potentiometrically. Since the e.m.f. of the cell is known and equal to the algebraic sum of the two electrode potentials, of which $\xi^0_{H_2}$ is zero, the potential of the other electrode is obtained. If ξ_x and $\xi^0_{H_2}$ are the oxidation potentials of the electrode and the standard hydrogen electrode respectively, the e.m.f. (E) of the cell will be given by the difference of the two.

i.e., $$E = \xi_x \sim \xi^0_{H_2}$$

If the given electrode functions as negative electrode then

$$E = \xi_{anode} - \xi_{cathode} = \xi_x - \xi^0_{H_2} = \xi_x, \text{ (since } \xi^0_{H_2} = 0)$$

But if the given electrode functions as positive electrode then

$$E = \xi_{anode} - \xi_{cathode} = \xi^0_{H_2} - \xi_x = -\xi_x$$

E, the emf of the cell is positive, the oxidation potential (ξ_x) of the electrode may be positive or negative, depending upon its relative position with the standard H_2-electrode.

(*i*) *Determination of the standard electrode potential* (ξ^0_{Zn}) *of zinc electrode.* Arrange the cell; $Zn \mid Zn^{++} (a_{Zn^{++}}) \parallel H^+(a_{H^+} = 1) \mid H_2(Pt)$ (1 atm)

In this cell zinc serves as negative electrode. The e.m.f. of the cell (E) is measured potentiometrically.

$$E = \xi_{Zn} - \xi^0_{H_2} = \left[\xi^0_{Zn} - \frac{RT}{nJ} \ln a_{Zn^{++}}\right] - 0 = \xi^0_{Zn} - \frac{RT}{nJ} \ln a_{Zn^{++}}$$

If the zinc sulphate solution taken has unit activity, then the measured emf of the cell would be the standard electrode potential of zinc, ξ^0_{Zn}. Otherwise, $a_{Zn^{++}}$ the activity of the Zn^{++} is separately measured to obtain the value of ξ^0_{Zn}.

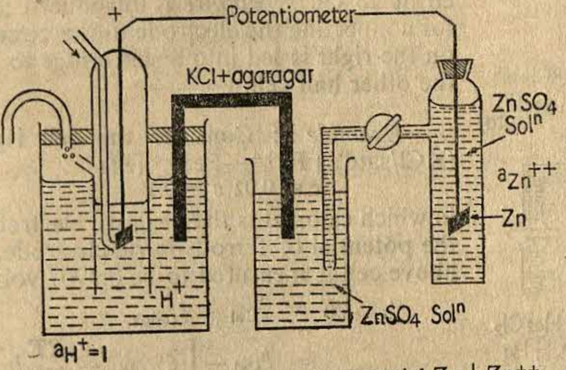


Fig. XXI.6. Detn. of electrode potential Zn | Zn^{++} from the e.m.f. of cell Zn | Zn^{++} || H^+ | H_2

At 25°C, with a Zn^{++}-ion solution of activity, ($a_{Zn^{++}} = 0.1$), the experimental value of the emf of this cell has been found to be 0.7914 volt.

$$\therefore \qquad E = \xi^0_{Zn} - \frac{RT}{2\mathcal{F}}\, ln\, a_{Zn^{++}} = \xi^0_{Zn} - \frac{0.0592}{2}\log(0.1)$$

$$\text{or} \qquad 0.7914 = \xi^0_{Zn} + 0.0296, \text{ whence } \xi^0_{Zn} = +0.7618 \text{ volt}$$

(*ii*) *Determination of the potential of calomel electrode*, $Hg-Hg_2Cl_2(s) \mid Cl^-$ When coupled with a standard H_2-electrode, the calomel electrode functions as the positive electrode. The cell is

$$(Pt)\,\overset{(-)}{H_2}(g) \mid H^+(C_{H^+}=1) \parallel \underset{C_{Cl^-}}{KCl\ Sol^n} \mid \overset{(+)}{Hg_2Cl_2}(s)-Hg$$

The emf of the cell, $E = \xi^0_{H_2} - \xi_{Calomel} = -[\xi_{Cal}]$

$$\text{or} \qquad E = -\left[\xi^0_{Cal} + \frac{RT}{n\mathcal{F}}\, ln\, C_{Cl^-}\right], \quad \text{see eqn. XXI.12.}$$

When $a_{Cl^-} = 1.0$, $E = -\xi^0_{Cal} = 0.2800$ volts (experimentally found).

Hence the standard potential of calomel electrode is −0.2800. The potentials of the colomel electrode with different concentrations of Cl^- are as follows:

Conc. of KCl	Saturated	1.0N	0.1N
ξ calomel (volts)	−0.2415	−0.2800	−0.3338

The use of standard H_2-electrode is often inconvenient as considerable difficulties arise in its preparation. Calomel electrodes are very stable and good reversible electrodes and are extensively used as secondary reference electrodes. They are also easily prepared. A stoppered glass-tube provided with side-tubes as shown in Fig. XXI.7 is taken. Pure mercury is placed in the bottom and it is then covered with a paste of mercurous chloride (calomel) and mercury. The electrolyte is a solution of KCl of known concentration (usually saturated at 25°C). A Pt-wire is introduced into the mercury for connecting the electrode to the circuit. The sidetube on the right is led into a salt bridge to be coupled with the other half cell.

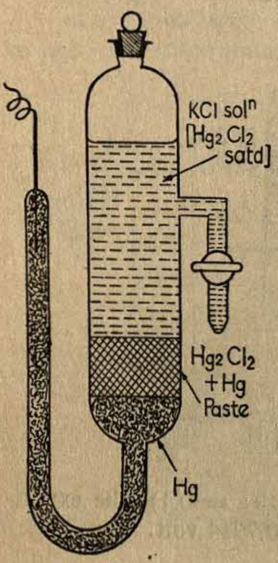


Fig. XXI.7
Calomel electrode

Example 5: Consider the cell Hg-$Hg_2Cl_2(s)$ | Cl^- (KCl/satd) ‖ Fe^{++}—Fe^{+++} (Pt)
$c = 0.02$ $c = 0.1$
in which calomel is the negative electrode. To determine the potential of ferrous-ferric electrode, the emf. of the above cell is measured to be 0.5707 volt at 25°C.

$$\therefore \quad E = \xi_{\text{Cal}} - \xi_{\text{redox}}$$

$$= \xi_{\text{Cal}} - \left[\xi^0_{\text{redox}} - \frac{RT}{\mathcal{F}} ln \frac{c_{\text{Fe}}{}^{+++}}{c_{\text{Fe}}{}^{++}} \right]$$

$$= \xi_{\text{Cal}} - \left[\xi^0_{\text{redox}} - 0.0591 \log \frac{0.1}{0.02} \right]$$

$$\therefore \quad 0.5707 = -0.2415 - \xi^0_{\text{redox}} + 0.0410$$

whence $\xi^0_{\text{Fe}^{++}, \text{Fe}^{+++}} = -0.771$ volt

Thus an electrode potential can be obtained by coupling it with a calomel electrode instead of a normal hydrogen electrode.

In the table appended below, the standard oxidation potentials of different electrodes are given. The electrodes at the top of the Table have a greater tendency to give up electrons. If a cell is built up with two electrodes from this list, one which is above in the list will be the negative electrode. The plus and minus signs arise as we have given arbitrarily a zero value to the normal H_2-electrode.

TABLE: STANDARD (OXIDATION) POTENTIALS (AT 25°C) OF SINGLE ELECTRODE (HYDROGEN SCALE)

Electrode	*Electrode Reaction*	*Electrode Potential ξ^0 (volts)*
K | K^+	K $= K^+ + \epsilon$	+ 2.925
Na | Na^+	Na $= Na^+ + \epsilon$	+ 2.714
Mg | Mg^{++}	Mg $= Mg^{++} + 2\epsilon$	+ 2.34
Zn | Zn^{++}	Zn $= Zn^{++} + 2\epsilon$	+ 0.761
Fe | Fe^{++}	Fe $= Fe^{++} + 2\epsilon$	+ 0.441
(Pt)Cr^{++}, Cr^{+++}	$Cr^{++} = Cr^{+++} + \epsilon$	+ 0.410
Cd | Cd^{++}	Cd $= Cd^{++} + 2\epsilon$	+ 0.402
Co | Co^{++}	Co $= Co^{++} + 2\epsilon$	+ 0.280
Ni | Ni^{++}	Ni $= Ni^{++} + 2\epsilon$	+ 0.240
Ag | AgI(*s*)/I^-	$Ag + I^- = AgI + \epsilon$	+ 0.152
Sn | Sn^{++}	Sn $= Sn^{++} + 2\epsilon$	+ 0.140
Pb | Pb^{++}	Pb $= Pb^{++} + 2\epsilon$	+ 0.126
(Pt)$\frac{1}{2}H_2(g)$—H^+	$\frac{1}{2}H_2 = H^+ + \epsilon$	+ 0.000

Electrode	*Electrode Reaction*	*Electrode Potential* ξ^0 *(volts)*
(Pt)Sn^{++}, Sn^{+++}	$Sn^{++} = Sn^{+++} + 2\epsilon$	− 0.15
Ag | $AgCl(s)/Cl^-$	$Ag + Cl^- = AgCl + \epsilon$	− 0.2223
Hg | $Hg_2Cl_2(s)/Cl^-$	$2Hg + 2Cl = Hg_2Cl_2 + 2\epsilon$	− 0.2800
Cu | Cu^{++}	$Cu = Cu^{++} + 2\epsilon$	− 0.337
I_2 | I^-	$2I^- = I_2 + 2\epsilon$	− 0.535
(Pt)Fe^{++}, Fe^{+++}	$Fe^{++} = Fe^{+++} + \epsilon$	− 0.771
Ag | Ag^+	$Ag = Ag^+ + \epsilon$	− 0.799
Br_2 | Br^-	$2Br^- = Br_2 + 2\epsilon$	−1.0652
(Pt)Tl^+, Tl^{+++}	$Tl^+ = Tl^{+++} + 2\epsilon$	− 1.250
Au | Au^{+++}	$Au = Au^{+++} + 3\epsilon$	− 1.300
Cl_2 | Cl^-	$2Cl^- = Cl_2 + 2\epsilon$	− 1.359
(Pt) Ce^{+++}, Ce^{++++}	$Ce^{+++} = Ce^{++++} + \epsilon$	− 1.610

Example 6. Write the reaction in the following cell and find out the free-energy change in the process under standard conditions: (Pt)$Tl^+ - Tl^{+++}$ || Cu^{++}|Cu

Given: $\xi^0_{Tl^+/Tl^{+++}} = -1.250$, and $\xi^0_{Cu/Cu^{++}} = -0.337$

Since ξ^0_{Cu} is higher, the copper electrode would be the negative electrode and the cell reaction would be

$$Cu + Tl^{+++} \rightarrow Cu^{++} + Tl^+$$

The standard e.m.f. of the cell is

$$E^0 = \xi^0_{Cu} - \xi^0_{Tl^+/Tl^{+++}} = -0.337 - (-1.250) = 0.913$$

$$\therefore \text{ Free energy change } \triangle G^0 = -nJE^0 \text{ volt. coulombs}$$

$$= \frac{-2 \times 96500 \times 0.913}{4.2} \text{ calories} = -41.95 \text{ Kcal}$$

21.9. Liquid Junction Potential

In electrochemical cells of the type, Zn | $ZnSO_4$ Soln || $CuSO_4$ Soln | Cu, two different solutions come in contact. At the junction of the two liquids, a potential difference, called the *liquid Junction potential*, arises. This is because the speeds of the different ions of the two electrolytes diffusing are different. The faster ions move across the boundary ahead of the slower. So one side of the boundary becomes positively charged and the other negatively creating a double layer at the junction of the two liquids. At the junction of the two electrolytes therefore exists a potential difference.

In the treatment of emf of galvanic cells, we have not so far considered the liquid junction potential. In fact, it has always been eliminated by inserting a **Salt bridge** between the two electrolytes (See Fig. XXI.6). It is a tube filled with agar-agar jelly saturated with KCl which connects the two half-cells. The elimination of the liquid junction potential is indicated by a pair of vertical lines while writing.

21.10. Concentration Cells

There is another type of cell in which the e.m.f. arises not due to any chemcal reaction but due to transfer of matter from one half-cell to the other owing to a concentration difference. These cells are called *concentration cells.* The concentration cells are of two kinds: (1) *Amalgam cells* and (2) *Electrolyte concentration cells.*

(*i*) **Amalgam Cells.** In amalgam cells two like electrodes of different concentrations are dipped in the same solution of an electrolyte containing an ion of the electrode material. Thus if two amalgams of silver of different concentrations be in contact with a silver nitrate solution, as

$$\underset{(c_{Ag} = c_1)}{\text{Ag(Hg)}} \;\Big|\; \text{AgNO}_3 \text{ soln} \;\Big|\; \underset{(c_{Ag} = c_2)}{\text{Ag(Hg)}}$$

then it is an electrode concentration cell. The concentrations of silver in the two amalgams are different. Since in majority of cases metals are used as electrodes and to have them in different concentrations these are taken in the form of amalgams, hence the name *amalgam cells.*

In this concentration cell, let the concentrations of silver in the two amalgams be C_1 and C_2, such that $C_1 > C_2$. The concentration of the $AgNO_3$ solution is C. The negative electrode is found to be the amalgam with a higher concentration of silver.

	Process	*Electrode potential*
At the −ve electrode	$Ag \rightarrow Ag^+ + \epsilon$;	$\xi_1 = \xi^0 - \frac{RT}{J} ln \frac{C}{C_1}$
At the + ve electrode	$Ag^+ + \epsilon \rightarrow Ag$;	$\xi_2 = -\left[\xi^0 - \frac{RT}{J} ln \frac{C}{C_2}\right]$

$$\text{The cell emf } E = \xi_1 + \xi_2 = \frac{RT}{J} ln \frac{C_1}{C_2}$$

The net result is the transport of a mole of Ag from the anode to the cathode.

(*ii*) **Electrolyte Concentration Cells.** In this type of cells, the electrodes on the two sides are the same but they are dipped into solutions differing in the concentrations of the reversible ion; such as,

$$\underset{(C_{Ag^+} = C_1)}{\text{Ag}-\text{AgNO}_3 \text{ soln}} \;\Big\|\; \underset{(C_{Ag^+} = C_2)}{\text{AgNO}_3 \text{ soln} - \text{Ag}}$$

Both the electrodes in such a cell would be of the same material but the potentials of the two electrodes will not be the same as the concentrations of the reversible ions in the two solutions are not the same.

In drawing current from such a cell the two electrodes will operate in opposition. If we take the $AgNO_3$-concentration cell, at one electrode silver will be deposited while silver will be dissolved in the other and the process will continue until the concentrations in the two solutions become equal. Let us denote the concentrations of Ag^+ in the two solutions by C_1 and C_2 such that $C_2 > C_1$. In the natural process of attaining equilibrium, silver will be deposited on the electrode in the more concentrated solution, where, therefore, the process is one of reduction, If ξ_1 and ξ_2 denote the oxidation potentials of the electrodes, then the net e.m.f. of the cell will be

$$E = \xi_1 - \xi_2 = \left(\xi_1{}^0 - \frac{RT}{nJ} \ln C_1\right) - \left(\xi_2{}^0 - \frac{RT}{nJ} \ln C_2\right)$$

Since, the same metal is used in both electrodes, $\xi_1{}^0 = \xi_2{}^0$

Hence, $$E = \frac{RT}{nJ} \ln \frac{C_2}{C_1} \qquad \text{...(XXI.15)}$$

21.11. Applications of Concentration Cells

(*a*) *Determination of valency.* The emf of an electrolytic concentration cell is given by

$$E = \frac{RT}{nJ} \ln \frac{C_2}{C_1} = \frac{0.0591}{n} \log \frac{C_2}{C_1}$$

If the emf (E) of a cell using known conc. C_2, C_1 of an electrolyte be measured, the valency (n) can be obtained.

The emf of the concentration cell using 0.5M and 0.05M Mercurous nitrate was found to be 0.029 volts.

$$\text{Hg} \mid \begin{array}{c}\text{0.05 M mercurous}\\ \text{nitrate}\end{array} \parallel \begin{array}{c}\text{0.5 M mercurous}\\ \text{nitrate}\end{array} \mid \text{Hg}; \quad E = 0.029 \text{ volts}$$

$$\therefore \quad 0.029 = \frac{0.0591}{n} \log \frac{0.5}{0.05}, \quad \text{whence } n = 2$$

(*b*) *Determination of solubility product.* The ionic concentration in a *saturated solution* can be obtained from emf of a concentration cell. If the salt in the electrolyte be sparingly soluble, it is assumed as completely dissociated. To illustrate, let us take the cell,

$$\overset{-}{\text{Ag}} \left| \begin{array}{c}\text{Saturated AgCl}\\ C_{\text{Ag}^+} = C_1\end{array} \right\| \begin{array}{c}\text{AgNO}_3 \text{ soln}\\ C_{\text{Ag}^+} = 0.01\end{array} \left| \overset{+}{\text{Ag}} \right.$$

The emf of the cell, $$E = \frac{0.0591}{1} \log \frac{C_2}{C_1} = 0.0591 \log \frac{0.01}{C_1}$$

Thus, the concentration of Ag^+ ions (C_1) in the saturated solution is known. The solubility product of AgCl $= C_1{}^2$.

(*c*) *Determination of transition pt. of a metal.* If two allotropes of a metal (say grey and white tin) be made electrodes of a cell with a single electrolyte (ammon. stannic chloride soln), then there will be a potential difference between these two electrodes except at the transition pt. At the transition pt. the two forms are in eqm, hence emf is zero. By slowly changing the temperature, the emf is measured until it vanishes. The transition temperature for tin is found to be 18°C.

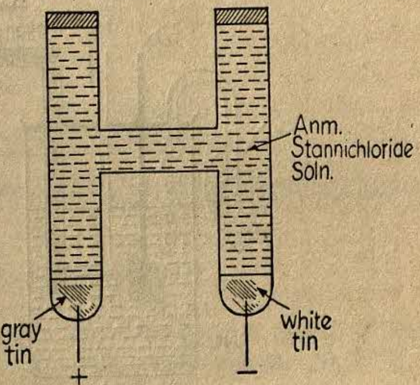


Fig. XXI.8
Det. of transition pt. of grey and white tin

21.12. Determination of pH from emf measurements

The hydrogen ion concentration of a solution (C_{H^+}) is conveniently expressed in terms of pH. The negative of the logarithm of H^+ activity is defined as pH;

$$\text{pH} = -\log a_{H^+}, \quad \text{or} \quad a_{H^+} = 10^{-\text{pH}}$$

In dilute solutions, $a_{H^+} \approx C_{H^+}$, hence $\text{pH} = -\log C_{H^+}$

The pH of a solution is ascertained very accurately from emf measurements. The given solution is made the electrolyte of a hydrogen electrode. The solution is taken in a pyrex glass vessel provided with a lid. At pt-foil coated with platinum black is kept immersed in the solution and pure H_2-gas at 1 atm. is continuously bubbled so that the pt-black and the solution are completely saturated and are at eqm. with the gas [Fig. XXI.9(a)]. Precautions are taken to prevent any diffusion of air. This is indeed a H_2-electrode, whose potential (ξ_{H_2}) is given by

$$\xi_{H_2} = \xi^{\circ}_{H_2} - \frac{RT}{J} \ln C_{H^+} = -\frac{RT}{J} \ln C_{H^+} \qquad (\text{since } \xi^{\circ}_{H_2} = 0)$$

This is then coupled with a reference electrode, such as standard H_2-electrode, calomel electrode etc. The emf of the cell is then measured, from which the C_{H^+} is known.

$$(\text{Pt})\ H_2 \left| \begin{matrix} H^+ \\ C = 1 \end{matrix} \right\| \begin{matrix} H^+ \\ C = C_{H^+} \end{matrix} \left| H_2\ (\text{Pt}) \right.$$

It is indeed a concentration cell; its emf (at 25°C),

$$\begin{aligned} E &= \xi_{H_2\,(\text{soln})} - \xi^{\circ}_{H_2} \\ &= \xi^{\circ}_{H_2} - \frac{RT}{J} \ln C_{H^+} - \xi^{\circ}_{H_2} = -\frac{RT}{J} \ln C_{H^+} \\ &= -2.303 \frac{RT}{J} \log C_{H^+} = 2.303 \frac{RT}{J} \text{pH} = 0.0591 \text{ pH} \end{aligned}$$

Since E is measured, hence pH of the solution is known.

(2) *Measurement with calomel electrode.* The arrangement is shown in Fig. XXI.9. A satd. calomel electrode is coupled with the H_2-electrode containing the solution through a salt-bridge.

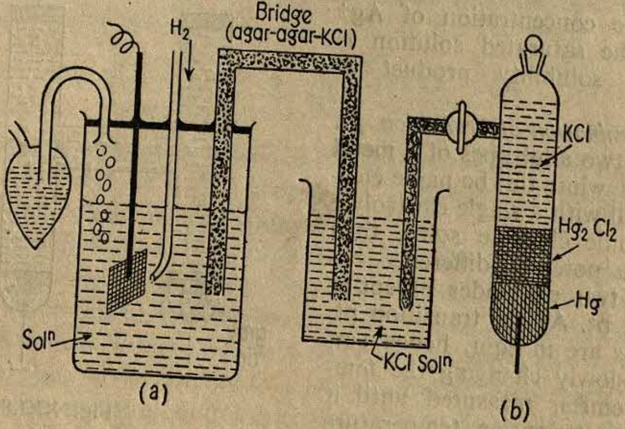


Fig. XXI.9. pH det. using Calomel electrode

The emf of the cell,

$$E = \xi_{H_2} - \xi_{cal}$$

$$= -\frac{RT}{J}\, ln\, C_{H^+} - \xi_{cal}$$

$$= 0.0591\ \text{pH} - (-0.242)\ \text{volts}$$

$$\text{or}\quad \text{pH} = \frac{E - 0.242}{0.0591}\quad (\text{at } 25°\text{C})$$

E is potentiometrically measured and hence pH is known.

(3) *Measurement with glass electrode:* The glass electrode consists of a thin membrane of a specially prepared soft glass globe containing a dilute solution of HCl, in which is immersed Ag—AgCl electrode;

Ag—AgCl (*s*) | 0.1N HCl | Glass | unknown solution

The potential of the glass electrode is given by

$$\xi_G = \xi_G^\circ + 0.0591\ \text{pH}\quad (\text{at } 25°\text{C})$$

It means that this glass electrode functions in the same way as a hydrogen electrode. The emf of the cell is

$$E = \xi_G - \xi_{cal} = \xi_G^\circ + 0.0591\ \text{pH} - \xi_{cal}$$

E is measured. Since ξ_G° is not known, *pH* can be ascertained after calibration with a standard.

(4) *Measurement with quinhydrone electrode:* Quinhydrone is an equimolecular compound of quinone and hydroquinone and when placed in a solution, the equilibrium is

$$C_6H_4(OH)_2 \rightleftharpoons C_6H_4O_2 + 2H^+ + 2\epsilon$$

This is indeed an oxidation-reduction system and if a Pt-wire is dipped in it, a redox single-electrode is formed. Writing 'Q' for $C_6H_4O_2$, we have

$$QH_2 \rightleftharpoons Q + 2H^+ + 2\epsilon$$

The equilibrium evidently depends upon the H^+ ion concentration. The emf of the single electrode potential is given by

$$\xi_Q = \xi_Q^\circ - \frac{RT}{2J}\cdot ln \frac{c_Q \cdot c_{H^+}^2}{c_{QH_2}}$$

$$= \xi_Q^\circ - \frac{RT}{2J}\cdot ln \frac{c_Q}{c_{QH_2}} - \frac{RT}{J}\, ln\, c_{H^+}$$

In the solution saturated with quinhydrone, the ration $\frac{c_Q}{c_{QH_2}}$ is maintained constant at unity, so that the electrode potential is

$$\xi_Q = \xi_Q^\circ - \frac{RT}{J}\, ln\, C_{H^+} = \xi_Q^\circ + 2.303\,\frac{RT}{J}\ \text{pH}$$

The potential therefore depends upon the H^+ ion activity. The value ξ° is predetermined with a solution of known H^+ ion concentration. At 25°C, $\xi_Q^\circ = -0.699$ volts.

To the given solution in a beaker is added a small quantity of quinhydrone and stirred well to ensure saturation. A bright Pt-foil is suspended in the solution, This is one half-cell which is connected through a salt bridge to the reference calomel electrode as

Hg | $HgCl_2(s)$ | Satd. KCl soln || (Q, QH_2 satd.) unknown soln | Pt

$$E = \xi_{cal} - \xi^{\circ}_{Q} - 2.303\frac{RT}{J}\text{pH}$$

The emf. E is measured and pH is thus evaluated since other quantities are known.

The quinhydrone electrode has many advantages over the hydrogen electrode. Its simplicity and quick attainment of reversible equilibrium are of utmost importance. A small quantity of solution is sufficient and air need not be excluded. It can also be used in presence of heavier ions or unsaturated organic substances where hydrogen electrode cannot be applied. But quinhydrone electrodes cannot be used in alkaline solutions above pH, 8.5.

Applications: The measurement of pH is useful in the determination of dissociation constants of acids, degree of hydrolysis of salts, etc. It has been shown earlier that the free energy change and the eqm constant of reactions can be evaluated for emf measurements. Quantitative estimation of salts, of acids, solubility of salts, ionic product of water, etc. can be made with the help of emf measurement (potentiometric titrations).

The knowledge of electrode potentials has also many applications. For example, the costly underground pipe-lines for conveying petroleum are subject to corrosion. This is prevented by using Magnesium-blocks attached to the pipe-lines at intervals and buried underneath. A small current is passed. Since magnesium has a higher oxidation potential, it serves as the anode and is preferentially corroded leaving iron pipe-line unaffected. The magnesium blocks are replaced from time to time.

Potentiometric Titrations: Various estimations are carried out by measuring emf. For example, chlorides are estimated by potentiometric titration with $AgNO_3$ solution. A known volume of NaCl solution is taken in a beaker in which is inserted a clean silver wire to act as an electrode, called 'indicator' electrode. From a burette the titrant $AgNO_3$ is added in small amounts. As silver chloride is formed there, we have a reversible electrode Ag | AgCl(s) | Cl^-. This is coupled with a reference electrode say a standard calomel electrode, *i.e.*,

Ag | AgCl(s) | Cl^- || calomel electrode

The emf,

$$E = \xi^{\circ}_{Ag/AgCl} - \frac{RT}{J}\ln\frac{C_{AgCl}}{C_{Ag}.C_{Cl^-}} - \xi^{\circ}_{Cal}$$

$$= \xi^{\circ}_{Ag/AgCl} - \xi^{\circ}_{Cal} + \frac{RT}{J}\ln C_{Cl^-}$$

Or $$E = \text{Constant} - \frac{RT}{J}\ln C_{Ag^+}$$

The solubility of AgCl is quite small, the concentration of Ag^+ ions in solution will change very slightly with the progress of the titration and hence the emf of the cell will change but little. But when the equivalence point is reached, even a drop of $AgNO_3$ added would bring about a large increase in the silver ion concentration and therefore a sharp change in the emf of the cell. In other words,

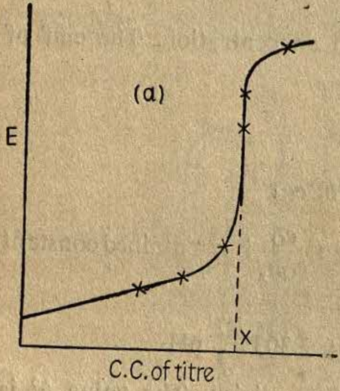


Fig. 10. Potention metric titrations

when the sharp change in emf is detected, the end-point is reached. A plot of emf of the cell against the volumes of $AgNO_3$ solution added is shown in Fig. XXI.10, from which the sudden change in slope is clearly noticed. The-point is thus easy to detect. The volume of the titre at the sharp break is noted, from which the conc. of the chloride is easily computed other precipitation reactions are used for similar estimations.

21.13. The Lead Accumulator or Acid Storage Cell

In this cell the negative electrode is lead and the positive electrode is lead with an adherent layer of PbO_2 on its surface. The electrolyte is H_2SO_4 (sp. gr. 1.15). The cell is

$$\overset{-}{Pb} \; \left| \; \begin{array}{c} H_2SO_4 \\ \text{(Saturated} \\ \text{withPbSO}_4\text{)} \end{array} \; \right| \; \overset{+}{PbO_2}(Pb)$$

(*i*) At the negative electrode, lead dissolves to form Pb^{++} ions, which then react with sulphate ions to be precipitated as sulphate.

$$Pb + SO_4^{--} \rightarrow PbSO_4 + 2\epsilon$$

(*ii*) At the positive electrode, the plumbic ion is reduced to Pb^{++} ions and ultimately lead sulphate is formed on the cathode as well.

$$PbO_2 + 4H^+ + SO_4^{--} + 2\epsilon \rightarrow PbSO_4 + 2H_2O$$

Hence the net result during discharge of the cell i.e. when it gives current, is

$$PbO_2 + Pb + 2H_2SO_4 \rightarrow 2PbSO_4 + 2H_2O$$

When the cell is discharged appreciably, *i.e.*, $PbSO_4$ formed at both electrodes, the cell is charged by passing a current from an external e.m.f. which reverses the chemical process, *i.e.*,

$$PbO_2 + Pb + 2H_2SO_4 \underset{\text{charge}}{\overset{\text{discharge}}{\rightleftharpoons}} 2PbSO_4 + 2H_2O$$

During charging Pb is deposited on the original anode and PbO_2 is formed on the cathode. H_2SO_4 is regenerated.

The anode potential would be

$$\mathcal{E}_1 = \mathcal{E}^0{}_{Pb/Pb^{++}} - \frac{RT}{2J} ln \frac{c_{Pb^{++}}}{c_{Pb}}, \qquad \mathcal{E}^0{}_{Pb/Pb^{++}} = 0.12$$

and the cathode potential (considering it as Pb^{4+}/Pb^{2+} electrode)

$$\mathcal{E}_2 = \mathcal{E}^0{}_{Pb^{++}/Pb^{++++}} - \frac{RT}{2J} ln \frac{c_{Pb^{++++}}}{c_{Pb^{++}}}, \quad \mathcal{E}^0{}_{Pb^{2+}/Pb^{4+}} = -1.74$$

Hence, the net emf of the cell is

$$E = \mathcal{E}_1 - \mathcal{E}_2 = \mathcal{E}^0{}_{Pb/Pb^{++}} - \mathcal{E}^0{}_{Pb^{++}/Pb^{++++}} + \frac{RT}{2J} ln \frac{c_{Pb^{++++}}}{c^2{}_{Pb^{++}}}$$

$$= 0.12 + 1.74 + \frac{RT}{2J} ln \frac{c_{Pb^{4+}}}{c^2{}_{Pb^{++}}} = 1.86 + 0.029 \log \frac{c_{Pb^{4+}}}{c^2{}_{Pb^{2+}}}$$

The emf is about 2.07 volts.

21.14. Polarisation

If a current is passed through two Pt-electrodes immersed in dilute H_2SO_4, hydrogen and oxygen are evolved at the cathode and anode respectively. The current in the external circuit flows from the cathode to the anode and from anode to cathode within the cell. If the battery be now removed and a galvanometer is inserted in the circuit, a current is observed to pass between the two electrodes but in an opposite direction, *i.e.* the current flows in the outer circuit from original anode to cathode. This is due to the fact that during electrolysis, the two electrodes become saturated with adsorption of hydrogen and oxygen evolved. They now function as hydrogen and oxygen electrodes. The emf of this cell is opposite to that of the battery and is often mentioned as *back emf.* This phenomenon of generation of back emf from the products of electrolysis is called *polarisation.*

Similar situations occur with other such irreversible systems. For example, if copper and zinc electrodes are used for electrolysis of dilute H_2SO_4, the electrodes are soon converted into gas electrodes. On removing the battery, they exhibit a back emf.

21.15. Decomposition Potential and Overvoltage

If two Pt-electrodes be dipped in a dilute H_2SO_4 solution and a voltage of say 0.5 or 1.0 volt be applied between them, a current will start flowing but very soon it would come almost to a stop. This is due to the back emf which opposes the applied voltage. The applied voltage is then slowly increased, but the current strength would increase very slightly. When the applied voltage reaches a certain value, the current is found to increase rapidly with increase in the applied voltage. At this point *d*, (Fig. XXI.11), gas bubbles begin to evolve and continuous electrolysis starts and does not stop even if the voltage is kept constant. This is easily shown by plotting the current against applied voltage. *The voltage which just overcomes the back emf due to polarisation and allows continuous smooth decomposition is called the Decomposition Potential of the given electrolyte.*

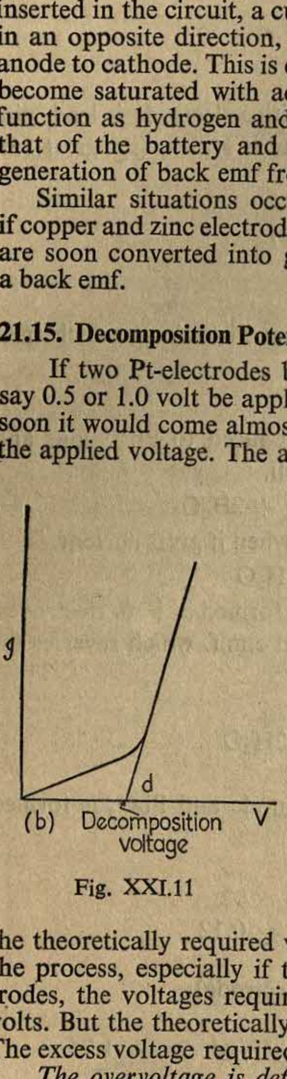


Fig. XXI.11

The decomposition potential of sulphuric acid and other acids as well as of alkalis is about 1.7 volts.

From the free-energy change of the reaction involved, the emf of a reversible cell can be easily obtained. But during actual electrolysis, the voltage required for decomposition is found to be higher than the theoretically required voltage. This is because some irreversibility enters into the process, especially if the products are gaseous. Thus, with Pt and Pb electrodes, the voltages required for decomposition of dil. H_2SO_4 are 1.7 and 2.2 volts. But the theoretically calculated value for this decomposition is 1.23 volts. The excess voltage required is called 'overvoltage'.

The overvoltage is defined as the difference between the voltage at which decomposition actually occurs during electrolysis and the theoretical value at which it should have occurred. The overvoltage depends not only on the electrolyte but also on the nature and material of the electrodes.

EXERCISES

1. What is the emf of a voltaic cell ? How is it experimentally measured ? Describe the standard cell which you would use in this measurement.

2. Establish thermodynamically a relation between the emf of a cell and the free-energy change of the chemical reaction involved. How would you find out the enthalpy change and entropy change of the process from emf measurements?

3. (*a*) Define Half-cell and standard electrode potential of an electrode. Give examples to show that the emf of a cell can be computed from the electrode potentials of the electrodes of the cell. (*b*) Classify the different types of electrodes. Give a general equation for the potentials of these electrodes.

4. At 25°C, show that $E = E^\circ - \frac{0.0591}{n} \Sigma \nu \log C$. Can you determine the eqm. constant from emf data?

5. Give expressions for the emf of the following cells:

(*i*) $Pt(H_2) \mid H^+ \parallel Ag^+ \mid Ag$

(*ii*) $Fe \mid Fe^{++} \parallel Cl^- AgCl(s) \mid Ag$

(*iii*) $Mg \mid Mg^{++} \parallel$ Calomel electrode

6. Deduce an expression for the 'redox potentials' of an electrode and explain it. What would be the expressions of the emf of the following cells:

(*i*) $Hg \mid Hg_2Cl_2(s) \mid Cl^- \parallel Fe^{++}, Fe^{+++}$ (Pt)

(*ii*) (Pt) $Fe^{++}, Fe^{+++} \parallel Ce^{+++}, Ce^{++++}$ (Pt)

7. Write explanatory notes on the following electrodes and give expressions for their potentials:

(*i*) chlorine electrode (*ii*) quinhydrone electrode (*iii*) calomel electrode (*iv*) glass electrode.

8. The standard electrode potential of Zn is + 0.76 volts. Determine the potential of the zinc electrode immersed in 0.1M $ZnSO_4$ solution at 25°C, assuming $ZnSO_4$ fully ionised in solution. (Sivaji Univ. '71) [Ans. 0.7896 volts]

9. What do you understand by a hydrogen electrode? Why is the calomel electrode often used instead of the standard hydrogen electrode? How would you determine the potential of a calomel electrode?

10. What do you mean by a hydrogen electrode? Describe any two methods for the determination of the hydrogen ion concentration of a solution. (Madurai Univ.)

11. Write down the electrode reaction and calculate the oxidation potential of each of the following at 25°C:

(*i*) $Ag/AgCl(s) \mid Cl^-(a = 0.0001)$; $\xi^0 = -0.2225$

(*ii*) $H_2(g)/1$ atm $\mid H^+(a = 0.15)$

Calculate the potential of the cell obtained by combining (*i*) and (*ii*) above. (Viswa Bharati Univ.) [Ans. −0.4589; 0.0487; 0.5076 volts]

12. What is a concentration cell? Derive an expression for the emf of such a cell. Indicate some applications of the concentration cells.

13. Calculate the potential of a copper electrode dipped in 0.1M solution of $CuSO_4$ solution (fully dissociated) at 25°C. The electrode potential $Cu^{++}/Cu = -0.34$ volts. (Punjab Univ.) [Ans. −0.3696 volt]

14. Write notes on: (*i*) polarisation (*ii*) overvoltage (*iii*) amalgam electrodes (*iv*) quinhydrone electrode (*v*) redox potential.

15. The cell, $Hg \mid Hg_2Cl_2(s) \mid KCl(1.0M) \parallel$ quanhydrone (Pt), had an emf of 0.212 volt at 25°C. Calculate the *pH* of the solution. The potential of the normal calomel electrode is −0.2812 volt and ξ° for quinhydrone electrode is −0.6996 volt. (Bangalore Univ.) [Ans. $pH = 3.5$]

16. The emf of a cell consisting of a hydrogen electrode and the normal calomel electrode is 0.664 volts at 25°C. The potential of the normal calomel electrode is -0.2812 volt. Calculate the *pH* of the solution containing the hydrogen electrode. (Bangalore Univ.) [**Ans.** $pH = 6.5$]

17. What is the emf of the cell: $Pb \mid Pb^{++} (a = 1) \parallel Ag^{+} (a = 1) \mid Ag$? Given the standard reduction potential (at 25°C) of the lead electrode is -0.125 volt and that of silver electrode is $+ 0.799$ volt. (Madras Univ.) [Ans. 0.924 volt]

18. Derive an expression for the emf of the galvanic cell

$$(Pt)\ H_2\ (1\ atm) \mid HCl\ (c_1) \parallel AgCl(s) \mid Ag$$

In what ways can the measurement of emf be used for determining *pH* of solution? (Gauhati Univ.)

CHAPTER 22

IONIC EQUILIBRIUM
ACIDS AND BASES

22.1. Dissociation Constants of weak acids and bases

The weak acids and bases are only partially dissociated in solution and there is an equilibrium between the ions and the undissociated molecules. The extent or *degree of dissociation* (α) is the fraction of the total number of molecules dissociated into ions. As already mentioned earlier, the degree of dissociation of weak electrolytes increases with dilution. For the acid HA having concentration c,

$$\begin{array}{llll} & HA \rightleftharpoons & H^+ + & A^- \\ \text{Conc.} & (1-\alpha)c & \alpha c & \alpha c \end{array}$$

the eqm constant, generally called the *dissociation constant* (K_a) *of the acid* is given by (see Sec. 20-18),

$$K_a = \frac{c_{H^+} \times c_{A^-}}{c_{HA}} = \frac{\alpha c \times \alpha c}{(1-\alpha)c} = \frac{\alpha^2 c}{(1-\alpha)} \qquad \ldots \text{(XXII.1)}$$

This is called the *Ostwald's dilution law.*

The degree of dissociation is small and the solution is supposed to behave ideally, hence concentration terms are used in place of activities.

The dissociation constant of a weak base will also be similar. For,

$$BOH \rightleftharpoons B^+ + OH^-,$$

$$K_b = \frac{c_{B^+} \times c_{OH^-}}{c_{BOH}} = \frac{\beta^2 c}{1-\beta} \qquad \ldots \text{(XXII.2)}$$

where β is the degree of dissociation of the base.

TABLE: THE DISSOCIATION CONSTANTS OF ACETIC ACID AT 25°C

Conc. (C)	1.1×10^{-4}	1×10^{-3}	2.4×10^{-3}	5×10^{-3}	9.84×10^{-3}
$K_a \times 10^5$	1.75	1.75	1.75	1.72	1.75

The logarithmic values; pK_a and pK_b: The dissociation constants of acids and of bases are often expressed in their logarithmic forms, such that

$$pK_a = -\log_{10} K_a \quad \text{and} \quad pK_b = -\log_{10} K_b \qquad \ldots \text{(XXII.3)}$$

Approximations: When the acid (or base) is very weak or α is very small, we can write eqn. (XXII.1), as

$$K_a = \frac{\alpha^2 c}{1-\alpha} = \alpha^2 c\,; \qquad \text{or} \quad \alpha = \sqrt{\frac{K_a}{c}} \qquad \ldots \text{(XXII.4)}$$

The degree of dissociation is inversely proportional to the sq. root of the concentration. Further, *for a normal solution, the degree of dissociation is equal to the square root of the dissociation constant.*

Again, $$c_{H^+} = \alpha c = \sqrt{\frac{K_a}{c}} \cdot c = \sqrt{K_a c}$$

or $$-\log c_{H^+} = -\tfrac{1}{2}\log K_a - \tfrac{1}{2}\log c$$

i.e. $$\text{pH} = \tfrac{1}{2}pK_a - \tfrac{1}{2}\log c \qquad \ldots \text{(XXII.5)}$$

Polybasic acids. The polybasic acids have more than one ionisable hydrogen and these ionise in successive stages. The degrees of ionisation at different stages are different and the dissociation constants for successive dissociation are also different. For example:

$$H_3PO_4 \rightleftharpoons H^+ + H_2PO_4^- \quad (K_{a_1} = 7.5 \times 10^{-3})$$
$$H_2PO_4^- \rightleftharpoons H^+ + HPO_4^{--} \quad (K_{a_2} = 6.2 \times 10^{-8})$$
$$HPO_4^{--} \rightleftharpoons H^+ + PO_4^{---} \quad (K_{a_3} = 4.8 \times 10^{-13})$$

From the dissociation constants it is easy to find out the concentration of ions present in solution; say for concentration $H_2PO_4^-$ ion, $C_{H_2PO_4^-} \approx \alpha C = \sqrt{k_1 C}$. It can be shown that in a $M/50$ phosphoric acid solution,

$$C_{H_2PO_4^-} = 0.01, \quad C_{HPO_4^{--}} = 6 \times 10^{-8}, \quad C_{PO_4^{---}} = 3 \times 10^{-18}$$

approximately. That is, even in a moderately dilute phosphoric acid solution, the concentration of PO_4^{---} ions is negligibly small.

22.2. Determination of dissociation constant

The dissociation constant (K_a) can be evaluated in two ways: (*i*) by measuring the specific conductance (L) of the given acid solution or (*ii*) by measuring the *pH* of the given acid solution.

(*i*) If c be the concentration of the acid solution, then its equivalent conductance $\lambda = (L \times 1000)/c$. The equivalent conductance of the acid at infinite dilution, $\lambda_0 = l_c + l_a$.

From eqn. (XX.33), we know, $$K_a = \frac{\lambda^2 c}{\lambda_0(\lambda_0 - \lambda)}$$

Substituting λ and λ_0, the value of K_a is obtained.

(*ii*) The *p*H of the given solution (conc. c) is measured by any method described in Sec. 21.12. The hydrogen ion concentration $C_{H^+} = \alpha c$ is known, because pH $= -\log C_{H^+}$. The degree of dissociation α is thus known.

Now $K_a = \frac{\alpha^2 c}{1-\alpha}$. Hence substitution of α would give the value of the dissociation constant. The dissociation constants of some acids and bases are given here.

TABLE: DISSOCIATION CONSTANTS OF ACIDS AND BASES AT 25°C

Acid/Base	*Formula*	*K_a or K_b*	*pK_a or pK_b*
Formic	$HCOOH$	1.77×10^{-4}	3.75
Acetic	CH_3COOH	1.8×10^{-5}	4.75
Benzoic	C_6H_5COOH	6.4×10^{-5}	4.2
Phenol	C_6H_5OH	1.2×10^{-10}	9.92
Hydrocyanic	HCN	7.2×10^{-10}	9.14
Iodic	HIO_3	1.7×10^{-1}	0.77
Hydrogen sulphide	H_2S	$K_1 = 9 \times 10^{-8}$	7.1
		$K_2 = 1 \times 10^{-15}$	15.00
Carbonic	H_2CO_3	$K_1 = 4.3 \times 10^{-7}$	6.4
		$K_2 = 5.6 \times 10^{-11}$	10.3
Oxalic	$(COOH)_2$	$K_1 = 5.9 \times 10^{-2}$	1.23
		$K_2 = 6.4 \times 10^{-5}$	4.19
Phosphoric	H_3PO_4	$K_1 = 7.5 \times 10^{-3}$	2.12
		$K_2 = 6.2 \times 10^{-8}$	7.2
		$K_3 = 5 \times 10^{-13}$	12.3
Citric	$C_2H_5.(COOH)_3$	$K_1 = 9.2 \times 10^{-4}$	3.02
		$K_2 = 2.69 \times 10^{-5}$	4.6
		$K_3 = 1.4 \times 10^{-6}$	5.9
Ammonium hydroxide	NH_4OH	1.8×10^{-5}	4.75
Methyl amine	CH_3NH_2	4.38×10^{-4}	3.36
Ethyl amine	$C_2H_5NH_2$	4.6×10^{-4}	3.34
Pyridine	C_6H_5N	1.4×10^{-9}	8.85
Aniline	$C_6H_5NH_2$	4.0×10^{-10}	9.40

Example 1. Calculate the pH of 0.01*M* benzoic acid.

From the table $pK_a = 4.2$, hence $\text{pH} = \frac{1}{2}pK_a - \frac{1}{2}\log C = \frac{1}{2}(4.2) - \frac{1}{2}\log 10^{-2}$
$= 3.1$

22.3. Common ion effect

The presence of an ion common with one of those produced by dissociation will depress the degree of dissociation of a weak acid or base. Let us consider the dissociation of the weak acetic acid.

$$CH_3COOH \rightleftharpoons H^+ + CH_3COO^-$$

Putting 'Ac' for CH_3COO, the dissociation constant

$$K_a = \frac{C_{H^+} \times C_{AC^-}}{C_{HAC}}$$

If now some HCl is added to it, the concentration of H^+-ions (C_{H^+}) will increase. In order to maintain the constancy of K_a, the concentration of acetatate ions (C_{AC^-}) must fall. This means that acetate ions would combine with H^+ ions to produce undissociated HAc. That is, the dissociation of acetic acid is suppressed. If instead of HCl, sodium acetate be added (acetate ion being common) the dissociation would be similarly depressed.

Ammonia is a weak base; $NH_4OH \rightleftharpoons NH_4^+ + OH^-$

$$K_b = \frac{C_{NH_4^+} \times C_{OH^-}}{C_{NH_4OH}}$$

If some NH_4Cl be added, $C_{NH_4^+}$ increases, hence C_{OH^-} would decrease to maintain the constancy of K_b. That means the dissociation of NH_4OH would be depressed.

The suppression of the dissociation of a weak acid or a weak base when a solution containing a common ion is added is known as the *common ion effect.*

Example 2. The ionisation constant of HCN $= 4 \times 10^{-10}$. Calculate the conc. of H^+-ions in (*a*) $0.2M$ solution of HCN and (*b*) $0.2M$ solution of HCN containing 1 mole/litre of KCN. (Delhi Univ.)

(*a*) The degree of dissociation, $\alpha = \sqrt{K_a/c}$ (eqn XXII.4)

$$\therefore \quad \alpha = \sqrt{4\times10^{-10}/0.2} = 4.5 \times 10^{-5}$$

$\therefore$ Conc. of H^+ ions, $C_{H^+} = \alpha.C = 0.2\times4.5\times10^{-5} = 9\times10^{-6}$ gm ion/litre.

(*b*) The conc. of CN^--ion from HCN is negligible compared to that from KCN in which $C_{CN^-} = 1.0$

$$\therefore \quad \frac{C_{H^+}\times C_{CN^-}}{C_{HCN}} = \frac{C_{H^+}\times1.0}{0.2} = 4\times10^{-10}$$

$$\text{or} \quad C_{H^+} = 8 \times 10^{-11} \text{ gm-ion/litre.}$$

This shows that the dissociation is much depressed due to the presence of the common ion.

Example 3. What is the effect of adding 0.25 gm-mole of NH_4Cl to a litre of $0.1M$ ammonium hydroxide solution on the degree of dissociation of the base? $K_{NH_4OH} = 1.8 \times 10^{-5}$.

In $0.1M$ NH_4OH solution, which is a very weak base,

$$\alpha = \sqrt{K_b/C} = \sqrt{1.8\times10^{-5}/10^{-1}} = 0.0135$$

$$\therefore \quad C_{OH^-} = C_{NH_4^+} = 0.00135, \quad C_{NH_4OH} = 0.0986$$

Let α' be the degree of dissociation when 0.25 gm-mole of NH_4Cl was added. Then

$$C_{NH_4^+} = 0.25, \quad C_{OH^-} = \alpha' C = 0.1\alpha', \quad C_{NH_4OH} = (1-\alpha')C \approx 0.1$$

since α' is quite small.

$$\therefore \quad \frac{C_{NH_4^+}.C_{OH^-}}{C_{NH_4OH}} = \frac{0.25\times0.1\alpha'}{0.1} = 1.8\times10^{-5}$$

$$\text{or} \quad \alpha' = 7.2\times10^{-5}, \qquad \therefore \; C_{OH^-} = 7.2 \times 10^{-6}$$

i.e., degree of dissociation is reduced from 1.35% to 0.0072%.

22.4. Ionic Product of Water

It has been shown in Sec. 20.19, that the product of the concentrations of H^+ ion and OH^- ion in any aqueous solution is constant and its value is 1.0×10^{-14} (at 25°C). This is called the *ionic product of water* (K_w).

$$K_w = C_{H^+}\times C_{OH^-} \qquad \ldots \text{(XXII.6)}$$

The method of its determination has already been discussed (Sec. 20.19). Its value also depends upon the temperature.

The equation (XXII.6) really suggests that in an aqueous medium, the product of the concentrations of H^+ and OH^- should be constant. If we are dealing, not with pure water, but a dilute aqueous solution, this relation is still valid. In an acid solution, there is a preponderance of H^+ ions but nevertheless there would be some OH^- ions, and the product of the two concentrations would be 1×10^{-14} at 25°C. Similarly in alkali solutions, there exist some H^+ ions. For example, in a $M/100$ HCl solution.

$$C_{OH^-} = \frac{C_{OH^-} \times C_{H^+}}{C_{H^+}} = \frac{K_w}{C_{H^+}} = \frac{1 \times 10^{-14}}{1 \times 10^{-2}} = 1 \times 10^{-12}$$

22.5. pH and pOH

As already stated earlier, the concentration of H^+ ions is generally expressed in a logarithmic form such that the negative exponents may be dispensed with. The negative of the logarithm of H^+ ion concentration is defined as pH of the solution.

$$pH = -\log C_{H^+}, \quad \text{or} \quad C_{H^+} = 10^{-pH} \qquad \ldots (XXII.17)$$

For a solution pH $= 3$, $C_{H^+} = 10^{-3}$, and for a solution pH $= 8$, $C_{H^+} = 10^{-8}$

In the same way, the concentration of OH^--ions is expressed in pOH scale, defined as,

$$pOH = -\log C_{OH^-}, \quad \text{or} \quad C_{OH^-} = 10^{-pOH}$$

Again we know, $\quad C_{H^+} . C_{OH^-} = K_w$

or $\quad -\log C_{H^+} - \log C_{OH^-} = -\log K_w$

or $\quad pH + pOH = pK_w = \text{Constant.}$

Hence as pH increases, pOH must decrease and *vice versa*.

$$pK_w = -\log k_w = -\log (1 \times 10^{-14}) = 14 \text{ (at 25°C).}$$

or $\quad pH + pOH = 14$

In pure water, which is neutral, $C_{H^+} = C_{OH^-} = 10^{-7}$ *i.e.*, pH of water is 7.

Hence, the neutral solution has a pH $= 7$. Any solution having pH lower than seven will be acid and a solution having pH above seven will be alkaline. Thus at 25°C, pH = of $0.00001M$ KOH will be 9.0, for,

$$C_{H^+} = \frac{K_w}{C_{OH^-}} = \frac{10^{-14}}{10^{-5}} = 10^{-9}, \text{ i.e., } pH = 9$$

22.6. Generalised Concept of Acids and Bases

It would be useful now to mention briefly the modern ideas about acids and bases. Our general idea regarding acids and bases is based on Arrhenius concept in which an acid is defined as a compound which yields H^+ ions in aqueous solutions and a base is a compound yielding OH^- ions in aqueous solutions. Further, neutralisation of an acid with a base is really the union of H^+ and OH^- ions to form the solvent, water.

This definition though very useful in understanding acid base reactions has its limitations. For example, reactions illustrated below are certainly neutralisation reactions producing the solvent and salt and yet no H^+ or OH^- ion is involved:

(*a*) $NaNH_2 + NH_4Cl \rightarrow NaCl + 2NH_3$ (in liq. ammonia)

(*b*) $HCl + CH_3COONa \rightarrow CH_3COOH + NaCl$ (in glacial acetic acid)

Then again, in aqueous solution, acids such as $HClO_4$, HNO_3, H_2SO_4, HCl, etc. are all found completely dissociated and are regarded as almost equally strong. But when these acids are taken in glacial acetic acid medium, $HClO_4$ is found much stronger than nitric acid. Hence the solvent plays an important rôle in the manifestation of acid-base properties.

In 1923, Lowry and Brönsted advanced the protonic concept for acids and bases. According to this new concept, *an acid is defined as a substance which has a tendency to lose a proton* (H^+) *and a base is a substance which has a tendency to gain a porton.* The relationship between the two may be expressed as

$$A \rightleftharpoons H^+ + B$$

where A is the acid and B its *conjugate base*. To function as acid, it must have the corresponding conjugate base. A base must also have its conjugate acid.

$$\text{Acid} \rightleftharpoons \text{Proton} + \text{Congugate base}$$

$$HAc \rightleftharpoons H^+ + Ac^-$$

Acids and bases may be netural molecules or ions. A few examples are cited:

Acid	= *Proton*	+ *Base*
HCl	$\rightleftharpoons H^+$	$+ Cl^-$
NH_4^+	$\rightleftharpoons H^+$	$+ NH_3$
HCO_3^-	$\rightleftharpoons H^+$	$+ CO_3^{--}$
H_2O	$\rightleftharpoons H^+$	$+ OH^-$
HPO_4^{--}	$\rightleftharpoons H^+$	$+ PO_4^{---}$
$Cr(H_2O)_6^{+++}$	$\rightleftharpoons H^+$	$+ Cr(H_2O)_5OH^{++}$ etc.

The free proton is not likely to occur in solution. In water, the proton unites with a water molecule producing H_3O^+, hydronium ion. In some other solvents also, proton associates with solvent such as, $CH_3COOH_2^+$ (in glacial acetic acid), NH_4^+ ion (in liq. ammonia), $CH_3CH_2OH_2^+$ (in alcohol), etc.

In this text elsewhere, in treating the dissociation of acids, H^+ ion has been used as such for simplicity in writing equations, although properly H_3O^+ should have been used.

Water does function both as an acid and as a base. Water acts as an acid in presence of a base stronger than itself *e.g.*, ammonia; it gives protons to ammonia.

$$NH_3 + H_2O \rightarrow NH_4^+ + OH^-$$

But in presence of acids water behaves as a base accepting a proton,

$$HSO_4^- + H_2O \rightarrow H_3O^+ + SO_4^{--}$$

There are some other solvents which also play similar dualistic role in acid-base equilibria.

An acid will function as such only when it is in contact with some base *i.e.*, a proton acceptor. The base may be the solvent molecule as well. In other words, the acidic function will be manifest in presence of a solvent (S) with basic properties, such as,

$$HA + S = SH^+ + A^-$$

In fact, both S and A^- tend to accept the proton. The degree of acidity depends upon the relative capabilities of S and A^- in accepting the proton. An acid is strong when the tendency of the anion A^- to accept a proton is less than that of the solvent S, as in HCl. And the acid will be weak when the anion A^- is quite keen to accept the proton as in acetic acid. In the same way, a strong base is one having greater tendency to accept protons than the solvent molecules.

It is obvious that solvent would affect the acid-base character of a substance profoundly. From this point the solvents may be of four types:

Solvent	*Character*	*Examples*
(*a*) protophyllic	tendency to accept protons	NH_3, NH_2OH, RNH_2, etc.
(*b*) protogenic	tendency to release protons	H_2SO_4 HAc, HCOOH, HF, etc.
(*c*) amphiprotic	capable of both losing and gaining protons	H_2O, C_2H_5OH, etc.
(*d*) aprotic	no tendency either to lose or gain protons	C_6H_6, CCl_4, $CHCl_3$, etc.

Thus, HNO_3 acts as an acid in aqueous media losing a proton. But it behaves as a base by accepting a proton in anhydrous HF.

$$HNO_3 + HF \rightarrow H_2NO_3^+ + F^-$$

Again urea behaves as an acid in liquid ammonia but as a base in anhydrous formic acid,

$$NH_2CONH_2 + NH_3 \rightarrow NH_2CONH^- + NH_4^+$$
$$NH_2CONH_2 + HCOOH \rightarrow NH_2CONH_3^+ + HCOO^-$$

It is also evident that the interaction between an acid (HA) and a base (H_2O) leads to the formation of another acid (H_3O^+) conjugate to the base and a base (A^-) congugate to the acid. This is generally true.

$$\begin{array}{lllll}
\therefore & \text{Acid}_1 + & \text{Base}_2 & \rightleftharpoons & \text{Acid}_2 + \text{Base}_1 \\
\text{such as,} & \text{acid}_1 & \text{base}_2 & & \text{acid}_2 + \text{base}_1 \\
 & HAc + & H_2O & \rightleftharpoons & H_3O^+ + Ac^- \\
 & HCl + & H_2O & \rightleftharpoons & H_3O^+ + Cl^- \\
 & H_3O^+ + & NH_3 & \rightleftharpoons & NH_4^+ + H_2O \\
 & H_2O + & H_2O & \rightleftharpoons & H_3O^+ + OH^- \\
 & H_2O + & CN^- & \rightleftharpoons & HCN + OH^- \\
 & NH_4^+ + & CH_2COO^- & \rightleftharpoons & CH_3COOH + NH_3 \quad \text{etc.}
\end{array}$$

The beauty of the Lowry-Bronsted theory lies in the fact that it contains all effects of Arrhenius concept and further extends to include and explain other types of acid-base equilibria even in non aqueous media. A consideration of the dissociation constant will be more revealing.

Suppose we have an acid (HA) in aqueous medium,

$$HA + H_2O \rightleftharpoons H_3O^+ + A^-, \text{ then } K_a = \frac{a_{H_3O^+}.a_{A^-}}{a_{HA}} = \frac{a_{H^+}.a_{A^-}}{a_{HA}}$$

since the whole of proton is present as H_3O^+.

This is the same as the conventional dissociation constant. That is, Lowry-Brönsted concept gives the same result.

Lewis Acids: A more general theory for acids was advanced by Lewis on the basis of electron theory of valence. According to Lewis, an acid is a substance (molecule, ion or radical) which would readily accept a lone pair of electrons from a donor substance, which would be the base. Acid is thus an electron-pair acceptor and base is a donor of electron pair. Thus, the reaction, $Et_3N + BCl_3 \rightarrow Et_3N : BCl_3$ is definitely an acid-base neutralisation reaction which can be followed with an indicator in chlorobenzene solution. There is no proton, nor any OH group.

It is thus seen the neutralisation virtually means the formation of a co-ordinate linkage. To illustrate:

$$\begin{array}{llll} \textit{acid} & & \textit{base} & \\ \mathrm{H^+} & + & :\underset{\cdot\cdot}{\ddot{\mathrm{O}}}:\mathrm{H^-} & \rightarrow \mathrm{H}:\underset{\cdot\cdot}{\ddot{\mathrm{O}}}:\mathrm{H} \\ \mathrm{H^+} & + & :\underset{\cdot\cdot}{\ddot{\mathrm{S}}}:\mathrm{H^-} & \rightarrow \mathrm{H}:\underset{\cdot\cdot}{\ddot{\mathrm{S}}}:\mathrm{H} \\ \mathrm{SO_3} & + & \mathrm{CaO} & \rightarrow \mathrm{CaO}:\mathrm{SO_3} \end{array}$$

This theory covers all acids of the protonic concept and other substances too. The acidic properties of non-metallic oxides and the basic properties of metal oxides are also explained.

22.7. Relative strength of acids

The strength of an acid depends upon the effective concentration of the hydrogen ions and not on the total quantity of acid present per unit volume. To compare the strengths of two acids (HA_1 and HA_2), these are taken at the same concentration (C). If α_1 and α_2 be the degrees of dissociation then $\alpha_1 C$ and $\alpha_2 C$ are the concentrations of H^+ ions in them. Different methods are employed to find out the relative strengths of acids.

(*a*) **Conductivity method:** The degrees of dissociation are

$$\alpha_1 = \frac{\lambda_1}{\lambda_{0(1)}} = \frac{\lambda_1}{l_{H^+} + l_{A_1^-}} \quad \text{and} \quad \alpha_2 = \frac{\lambda_2}{\lambda_{0(2)}} = \frac{\lambda_2}{l_{H^+} + l_{A_2^-}}$$

But $\lambda_{A_1^-} \approx \lambda_{A_2^-}$ in most cases. Hence $\alpha_1/\alpha_2 = \lambda_1/\lambda_2$.

$$\text{Now,} \qquad \frac{\text{strength of } HA_1}{\text{strength of } HA_2} = \frac{\alpha_1 C}{\alpha_2 C} = \frac{\alpha_1}{\alpha_2} = \frac{\lambda_1}{\lambda_2}$$

The relative strength of the two acids is thus the ratio of their equivalent conductances, which are determined easily.

(*b*) **By Comparison of dissociation constants:** If K_1 and K_2 be the dissociation constants of the two acids HA_1 and HA_2, then

$$\alpha_1 = \sqrt{K_1/C} \quad \text{and} \quad \alpha_2 = \sqrt{K_2/C}$$

$$\therefore \qquad \frac{\text{strength of } HA_1}{\text{strength of } HA_2} = \frac{\alpha_1}{\alpha_2} = \sqrt{\frac{K_1}{K_2}}\text{; (concentration being same)}$$

This is especially true in the case of weak acids.

(*c*) **Catalytic Method:** The H+ ions act as catalyst in many organic reactions such as the hydrolysis of methyl acetate or of sucrose. The rate is given by

$$R = k_1 C_{H^+} . C_S \text{ , } (C_S \text{ is the conc. of the substrate}).$$

If two acids HA_1 and HA_2 be separately added in the same concentration of acid to a given solution of ester during its hydrolysis, then the ratio of their rates would be

$$\frac{R_1}{R_2} = \frac{k_1 C_{H^+(1)} . C_S}{k_1 C_{H^+(2)} . C_S} = \frac{C_{H^+(1)}}{C_{H^+(2)}} = \frac{\text{strength of } HA_1}{\text{strength of } HA_2}$$

Thus the relative strength of acids is known from the rates of hydrolysis.

(*d*) **From emf measurement:** If the pH of the solution of the two acids at the same concentration be measured, it would give the ratio of the concentration of the H+-ions and hence the ratio of their strengths.

$$\frac{\text{strength of } HA_1}{\text{strength of } HA_2} = \frac{C_{H^+(1)}}{C_{H^+(2)}} = \frac{10^{-pH(1)}}{10^{-pH(2)}} = 10^{pH(2)-pH(1)}$$

(*e*) **Distribution methods:** (*i*) **Thermal method** or **Thomson method.** In this method, the heats of neutralisation, q_1 and q_2, of the two acids HA_1 and HA_2 by NaOH or KOH are first determined separately. Then a mixture of 1 gm eqv. of HA_1 and 1 gm eqv. of HA_2 is taken and 1 gm eqv. of NaOH is added to the mixture. The heat evolved is measured and let it be q cal. Each acid will neutralise a fraction of NaOH proportional to its strength. Let us suppose x equivalents of NaOH is neutralised by HA_1, then HA_2 has neutralised $(1-x)$ equivalents of NaOH. The heat evolved would be $q_1 x + q_2(1-x) = q$

$$\text{or} \qquad x = \frac{q-q_2}{q_1-q_2} \text{ ; and } (1-x) = \frac{q_1-q}{q_1-q_2}$$

$$\therefore \qquad \frac{\text{strength of } HA_1}{\text{strength of } HA_2} = \frac{x}{1-x} = \frac{q-q_2}{q_1-q}$$

The relative strength of acids is known from the q-values.

(*ii*) **Ostwald's Volume–change method:** In this method, the volume change is noted (instead of thermal change) during neutralisation. Let v_1, v_2 be the volume-changes when HA_1 and HA_2 are separately neutralised by 1 gm eqv. of NaOH. Let v be the volume-change when 1 gm-equivalent of NaOH is added to a mixture containing 1 gm-eqv. HA_1 and 1 gm-eqv. HA_2. As before, if x equivalents of NaOH be neutralised by HA_1, then $(1-x)$ equivalents would be neutralised by HA_2.

$$\therefore \quad xv_1 + (1-x)v_2 = v,$$

$$\text{or} \quad x = (v-v_2)/(v_1-v_2); \quad \text{and} \quad (1-x) = \frac{v_1-v}{v_1-v_2}$$

$$\therefore \quad \frac{\text{strength of } HA_1}{\text{strength of } HA_2} = \frac{x}{1-x} = \frac{v-v_2}{v_1-v}$$

Example 4. The dissociation constants of acetic acid and cyanacetic acid are 1.8×10^{-5} and 3.6×10^{-3}. Compare their relative strengths.

Let S_1 and S_2 denote their strengths.

$$\therefore \quad \frac{S_1}{S_2} = \sqrt{\frac{K_1}{K_2}} = \sqrt{\frac{1.8 \times 10^{-5}}{3.6 \times 10^{-3}}} = 0.07$$

22.8. Isohydric Solutions

The dissociation of a weak electrolyte is generally suppressed to some extent by the addition of a common ion. But it is possible to mix two solutions of different weak acids without the dissociation of either being affected. Such acid solutions whose dissociations are not changed on mixing are said to be *isohydric* with one another.

Suppose two such weak acid solutions HA_1 and HA_2 have concentrations c_1 and c_2, in which their degrees of dissociation are α_1 and α_2. Let k_1 and k_2 be their dissociation constants. Then

$$k_1 = \frac{\alpha_1^2 c_1}{1-\alpha_1} \quad \text{and} \quad k_2 = \frac{\alpha_2^2 c_2}{1-\alpha_2}$$

Let v_1 litres of HA_1 solution be mixed with v_2 litres of HA_2 solution. On mixing, as degrees of dissociation remain constant and the total volume is $(v_1 + v_2)$, hence,

$$C_{H^+} = \frac{\alpha_1 c_1 v_1 + \alpha_2 c_2 v_2}{v_1 + v_2}, \quad C_{A_1^-} = \frac{\alpha_1 c_1 v_1}{v_1 + v_2}, \quad C_{HA_1} = \frac{(1-\alpha_1) c_1 v_1}{v_1 + v_2}$$

$$\therefore \quad k_1 = \frac{C_{H^+} . C_{A_1^-}}{C_{HA_1}} = \frac{(\alpha_1 c_1 v_1 + \alpha_2 c_2 v_2)\alpha_1}{(v_1 + v_2)(1-\alpha_1)}$$

Comparing with the earlier expression of k_1, we have

$$\alpha_1 c_1 v_1 + \alpha_2 c_2 v_2 = \alpha_1 c_1 (v_1 + v_2)$$

Similarly, considering the other acid HA_2, the expression would be

$$\alpha_1 c_1 v_1 + \alpha_2 c_2 v_2 = \alpha_2 c_2 (v_1 + v_2);$$

hence $\alpha_1 c_1 = \alpha_2 c_2 \quad$ *i.e.* $C_{H^+(1)} = C_{H^+(2)}$

Hence it is seen that two weak acid solutions would be isohydric when their hydrogen ion concentrations are the same before mixing. It depends in no way on the volumes of the solutions mixed. Such conditions may be extended to weak electrolytes having common ion other than acids which may be termed iso-ionic solutions.

Example 5. What should be the relative dilutions of acetic acid and cyanacetic acid so that the solutions would be isohydric? ($K_{\text{acetic}} = 1.8 \times 10^{-5}$, $K_{\text{cyan}} = 3.6 \times 10^{-3}$).

Let v_1 and v_2 be the dilutions of cyanacetic and acetic acids for isohydry. The condition for isohydry is $\alpha_1 C_1 = \alpha_2 C_2$, or $\alpha_1/v_1 = \alpha_2/v_2$

$$\text{i.e. } \alpha_1/\alpha_2 = v_1/v_2 \qquad \ldots\ldots (A)$$

From Ostwald's Law,

$$K_1 = \alpha_1^2 C_1 = \alpha_1^2/v_1$$

and

$$K_2 = \alpha_2^2 C_2 = \alpha_2^2/v_2$$

or

$$\frac{\alpha_1^2}{\alpha_2^2} = \frac{K_1 v_1}{K_2 v_2} \qquad \ldots\ldots (B)$$

Substituting from (A), $\frac{v_1^2}{v_2^2} = \frac{K_1 v_1}{K_2 v_2}$

or $\frac{v_1}{v_2} = \frac{K_1}{K_2} = \frac{3.6\times10^{-3}}{1.8\times10^{-5}} = 200 : 1$

22.9. Some Simple Calculations

Example 6. The eqv. conductance of a 0.001N weak monobasic acid is 48 mhos when the eqv. conductance at infinite dilution at 25°C is 390 mhos. Calculate the dissociation constant of the acid.

$$\alpha = \frac{\lambda}{\lambda_0} = \frac{48}{390} = 0.123; \text{ hence } 1-\alpha = 0.877$$

$$\therefore \quad K_a = \frac{\alpha^2 C}{1-\alpha} = \frac{(0.123)^2\times0.001}{0.877} = 1.73\times10^{-5}$$

Example 7. A 0.01 N solution of a monobasic acid dissociates to the extent of 10%. Calculate the dissociation constant of the acid. (Delhi Univ. 1976)

$$\alpha = 0.1, \qquad \text{conc. } C = 0.01$$

$$\text{Hence } K_a = \frac{\alpha^2 C}{1-\alpha} = \frac{(0.1)^2\times0.01}{1-0.1} = 1.1\times10^{-4}$$

Example 8. The dissociation constant of cyanacetic acid is 3.6×10^{-3}. Calculate the degree of dissociation and hydrogen-ion concentration of 0.01N solution of the acid.

Since the acid is a weak one, we have (eqn. XXII.4),

$$\alpha = \sqrt{K_a/C} = \sqrt{(3.6\times10^{-3})/0.01} = 0.60$$

The conc. of H⁺ ions, $C_{H^+} = \alpha\times C = 0.60\times0.01 = 0.006$ gm. eqv. per litre

Example 9. At 25°C, the degree of ionisation of a 0.1N weak acid solution is 0.012. What would the degree of ionisation of this acid at 25°C in a 0.01N solution?

Let α_1 be the degree of ionisation in 0.01N solution. Then

$$K_a = \alpha^2 C = (0.012)^2 \times 0.1 \text{ ; also } K_a = \alpha_1^2 C_1 = \alpha_1^2\times0.01$$

$$\therefore \quad \alpha_1^2 \times 0.01 = (0.012)^2 \times 0.1$$

$$\text{or} \qquad \alpha_1 = 0.038$$

The 0.01N acid solution will be 3.8% dissociated.

Example 10. Calculate the pH of a solution having a hydrogen ion concentration of 0.0048 gm-eqv./litre.

$$\text{pH} = -\log C_{H^+} = -\log [0.0048]$$

$$= -[\bar{3}.6812] = 2.319$$

Example 11. What will be the pH of a 0.002 N solution of a base assuming complete dissociation at 25°C?

$$C_{H^+} = \frac{K_w}{C_{OH^-}} = \frac{10^{-14}}{2\times10^{-3}} = 5\times10^{-12}$$

$$\therefore \quad \text{pH} = -\log(5 \times 10^{-12}) = 11.30$$

Example 12. Find out the pH of a 0.001 N acid solution if it be 4.0% ionised in this solution.

$$C_{H^+} = 0.001 \times 0.04 = 0.00004$$

$$\therefore \quad pH = -\log(4 \times 10^{-5}) = 4.301$$

Example 13. What will be the H+-ion concentration of solutions having (*i*) pH = 4.0 and (*ii*) pH = 9.8.

(*i*) $pH = 4$; *i.e.* $\log C_{H^+} = -4$

or $C_{H^+} = 10^{-4}$

(*ii*) $pH = 9.8$; *i.e.* $\log C_{H^+} = -9.8 = \overline{10}.2$

Taking antilogs; $C_{H^+} = 1.585 \times 10^{-10}$

Example 14. Calculate the pH of a 0.01*N* solution of an acid having a dissociation constant 1.8×10^{-5}. What will be the dissociation constant of the acid if the pH of the same solution = 2.7? (Delhi Univ. '75)

(*i*) $\alpha = \sqrt{K_a/C} = \sqrt{(1.8 \times 10^{-5})/0.01} = 4.24 \times 10^{-2}$

$\therefore \quad C_{H^+} = \alpha C = 4.24 \times 10^{-2} \times 0.01 = 4.24 \times 10^{-4}$

Hence, $pH = -\log(4.24 \times 10^{-4}) = 3.37$

(*ii*) $pH = 2.7$; *i.e.*, $\log C_{H^+} = -2.7 = \overline{3}.3$

From antilogs; $C_{H^+} = 2 \times 10^{-3}$

Now
$$K_a = \frac{C_{H^+} \times C_{A^-}}{C_{HA}} = \frac{(C_{H^+})^2}{(1-\alpha)C} \approx \frac{(C_{H^+})^2}{C}$$

$$= \frac{(2 \times 10^{-3})^2}{0.01} = 4 \times 10^{-4}$$

22.10. Buffer Solutions

If we add 1 c.c. of a 0.01*N* HCl to a litre of water, the pH of the solution changes from 7 to 5. But if we add the same to a litre of ammonium acetate solution, the pH practically remains unaltered at 7.0. The resistance of a solution to changes in H+ ion concentration upon the addition of small amounts of acid or alkali is termed 'buffer action'. Solutions which possess such properties are known as '*buffer solutions*', or simply, *buffers*. The buffer solutions have thus 'reserve acidity and reserve alkalinity'.

The buffer solutions usually consist of one of the following:

(*i*) A solution of a weak acid and its salt with a strong base, such as, acetic acid and sodium acetate.

(*ii*) A solution of a weak base and its salt with a strong acid, such as ammonium hydroxide and ammonium chloride.

(*iii*) A solution of an ampholyte (preferably with its salt). Ampholytes in solution act both as an acid and a base, by producing H+ ions or accepting H+-ions. The amino-acids such as glycine behaves in this fashion.

$$NH_2CH_2COOH \rightarrow {}^+NH_2CH_2COO^- + H^+;$$

$$NH_2CH_2COOH + H^+ \rightarrow {}^+NH_3CH_2COOH$$

In fact, glycine in aqueous solution remains as doubly-charged ions called *Zwitter ions*, $^+NH_3CH_2COO^-$.

Such solutions easily neutralise whether an acid or alkali be added.

The buffer action can be understood in the following way. Suppose we have a mixture of acid HA and its salt BA in solution. The ionisation equilibrium determines the H^+ ion concentration.

$$K_a = \frac{C_{H^+}.C_{A^-}}{C_{HA}} \quad \text{or} \quad C_{H^+} = \frac{C_{HA}}{C_{A^-}} K_a \qquad \ldots (A)$$

Also $K_w = C_{H^+} \times C_{OH^-}$

To the solution now if we add H^+ ions in the form of an acid, these H^+ ions would be removed as HA by combining with A^- of the salt. This is necessary to maintain the above ionisation equilibrium, and so pH remains practically undisturbed. On the other hand if some alkali is added to the buffer solution, the added OH^- ions disturb the ionisation equilibrium of water. To keep K_w constant OH^- ions and H^+ ions combine to form H_2O. In order to maintain acid ionisation equilibrium, some HA will dissociate to compensate for the H^+ ions removed. Here again the pH of the solution would remain at the initial level. In the same way, the buffering action of a mixture of weak base BOH and its salt BA can be explained. Such considerations are however applicable only when the added acid or alkali are not too large in comparison with the amounts of the salt or acid of the buffer.

Suppose a buffer is composed of an acid HA of concentration C_a and its salt BA of concentration C_s. Let C_{H^+} be the concentration of the H^+ ions in the buffer. Then, conc. of undissociated acid $C_{HA} = C_a - C_{H^+}$ and since the solution is electrically neutral, and the salt is assumed completely dissociated,

$$\text{conc. of anion, } C_{A^-} = C_S + C_{H^+}$$

Substituting these in (A) above,

$$C_{H^+} = K_a \frac{C_a - C_{H^+}}{C_S + C_{H^+}}$$

This quadratic equation when solved gives the value of the C_{H^+} of the buffer. But the acid is weak and further its dissociation is repressed by the salt, hence C_{H^+} is quite small compared to C_a or C_S. Hence

$$C_{H^+} \approx K_a. \frac{C_a}{C_S} = K_a. \frac{C_{acid}}{C_{salt}}$$

or
$$\text{pH} = pK_a + \log \frac{C_{salt}}{C_{acid}} \qquad \ldots (\text{XXII.8})$$

This equation, generally known as **Henderson equation** shows that pH of the buffer is governed by salt-acid ratio and the ionisation constant of the acid.

For a mixture of a weak base and its salt, similar treatment would show

$$C_{OH^-} = K_b . \frac{C_{base}}{C_{salt}}$$

or
$$\text{pOH} = pK_b + \log \frac{C_{salt}}{C_{base}} \qquad \ldots (\text{XXII.9})$$

The resistance to the change in pH on the addition of an acid or alkali is called '*Buffer action*'. The buffer action is measured by 'Buffer capacity, β'. It is the amount (b) of a strong base required to produce unit change in pH of the solution;

$$\beta = \frac{\mathrm{d}b}{\mathrm{d(pH)}}$$

The buffer capacity is maximum when the acid and the salt are present in equal concentrations. The pH of the buffer is then equal to pK_a (eqn. XXII.8).

When the ratio salt/acid is varied, the buffer will have a different pH, but not far away from the value of $\mathrm{p}K_a$. For example, if acid: salt = 1 : 4,

$$\mathrm{pH} = \mathrm{p}K_a + \log 4 = \mathrm{p}K_a + 0.60$$

But if the ratio acid to salt be 4 : 1, then

$$\mathrm{pH} = \mathrm{p}K_a + \log 1/4 = \mathrm{p}K_a - 0.60$$

The maximum variation in the acid: salt ratio allowed is 1 : 10 or 10 : 1. The limiting values of the buffer pH then are

$$\mathrm{pH} = \mathrm{p}K_a + \log \tfrac{1}{10} = \mathrm{p}K_a - 1 \quad \text{and} \quad \mathrm{pH} = \mathrm{p}K_a + \log \tfrac{10}{1} = \mathrm{p}K_a + 1;$$

$$\textit{i.e.,} \qquad \mathrm{pH} = \mathrm{p}K_a \pm 1$$

In other words, the acetate-acetic acid buffer is suitable in the pH range 4.74 + 1 and 4.74−1, *i.e.*, 5.74 ~ 3.74. [$\mathrm{p}K_a$ for acetic acid, 4.74]

In the laboratory buffers are extensively used. In analysis, different precipitations are carried out in specific pH-ranges for which buffering is required, for example, in precipitation of phosphates or their separations. Buffers are required in pH-determinations by colorimetric method, as also in standardisation of glass electrodes and other emf measurements. In the industrial chemical processes, various operations are pH-controlled, *e.g.*, electrodeposition of metals, tanning of leather, brewing of alcohols, manufacture of paper, baking, etc. The pH of the blood of normal human being is 7.4 and in internal applications of fluid etc. similar buffering is needed; in the study of soils also pH control is essential.

Some of the common buffers used in the laboratory with their pH-ranges:

Buffer solutions	pH-*range*
1. Glycine and glycine-HCl	1.0− 3.6
2. Phthalic acid and pot. acid. phthalate	2.2− 3.8
3. Acetic acid and Na-acetate	3.7− 5.57
4. Pot-acid phthalate and dipotassium phthalate	4.0− 6.2
5. Na_2HPO_4 and NaH_2PO_4	5.9− 8.0
6. Boric acid and borax	6.8− 9.2
7. Borax and NaOH	9.2−11.0

Example 15. The following buffer mixtures were prepared:
(a) 0.1M acetic acid and 0.01M sodium acetate per litre
(b) 100 c.c. of 0.1M acetic acid mixed with 100 c.c. of 0.1M potassium acetate.
Calculate their pH ($K_a = 1.8 \times 10^{-5}$).

$$(a)\ \text{pH} = \text{p}K_a + \log \frac{C_{\text{salt}}}{C_{\text{acid}}} = \text{p}K_a + \log \frac{0.01}{0.1}$$

$$\text{or pH} = \text{p}K_a - 1 = -\log(1.8\times10^{-5}) - 1 = 4.745 - 1 = 3.745$$

$$(b)\ \text{pH} = \text{p}K_a + \log \frac{C_{\text{salt}}}{C_{\text{acid}}}$$

$$\text{Since } C_{\text{acid}} = C_{\text{salt}} = 0.1/200, \quad \text{or} \quad \frac{C_{\text{salt}}}{C_{\text{acid}}} = 1$$

$$\therefore\ \text{pH} = \text{p}K_a + \log \frac{C_{\text{salt}}}{C_{\text{acid}}} = \text{p}K_a = 4.745$$

Example 16. The dissociation constant of ammonium hydroxide, $K_b = 1.8 \times 10^{-5}$ at 25°C. A buffer solution contains 0.025 mole NH_4OH and 0.035 mole NH_4Cl per litre. Calculate pH-value of the buffer.

$$K_b = 1.8\times10^{-5}, \quad \therefore\ \text{p}K_b = -\log(1.8 \times 10^{-5}) = 4.745$$

$$\text{From eqn. (XXII.9), pOH} = \text{p}K_b + \log \frac{C_{\text{salt}}}{C_{\text{base}}} = 4.745 + \log \frac{0.035}{0.025}$$

$$= 4.745 + 0.1462 = 4.891$$

$$\text{At 25°C, pH} + \text{pOH} = \text{p}K_w = 14$$

$$\therefore \quad \text{pH} = 14 - \text{pOH} = 14 - 4.891 = 9.109$$

SALT HYDROLYSIS

22-11. Hydrolysis of Salt Solutions

The solutions of *neutral* salts in water are not often found neutral in reaction. In many cases such aqueous solutions of salts are either alkaline or acidic to litmus. Thus a solution of ammonium chloride is acidic and a solution of potassium cyanide alkaline to litmus. This is due to the fact that at least a portion of the salt reacts with water to produce back the acid and the base from which the salt was obtained, *i.e.*, a process opposite to that of neutralisation occurs. This process of decomposition of the salt by water is *hydrolysis.* If the acid and the base produced by hydrolysis are not both strong, in other words if one of them be weak, their strengths would be different. The ionisation of the acid and base being unequal, the resulting solution due to hydrolysis would be acidic or alkaline. Consider, for example, a salt BA, which reacts with water as

$$BA + H_2O \rightleftharpoons BOH + HA$$

If BOH is a strong base and HA a weak acid, then BOH will produce large quantities of OH^- but HA will remain practically undissociated. The resulting solution will be alkaline. Similarly, if BOH is weak and HA is strong, it is obvious the solution will be acidic. If both the parent acid and base of the salt are strong, no hydrolysis would occur and the solution would be neutral as in the case of NaCl.

There are three distinct groups of salts suffering hydrolysis, for which the extent of hydrolysis may be considered separately;

(*a*) salts of strong acid and weak base
(*b*) salts of weak acid and strong base
(*c*) salts of weak acid and weak base.

Salts, being strong electrolytes, are supposed to be practically completely ionised in dilute solutions.

(*a*) **Salts of Strong Acid and Weak Base.** Let BA be such a salt which hydrolyses partly with water and suppose the degree of hydrolysis is x, which is usually small.

$$\underset{\text{salt}}{B^+ + A^-} + H_2O \rightleftharpoons BOH + HA \rightleftharpoons \underset{\text{base}}{BOH} + \underset{\text{acid}}{H^+ + A^-}$$

The acid, being strong and present in small concentration, is supposed to be fully ionised. Hence we may write,

$$B^+ + H_2O \rightleftharpoons BOH + H^+$$

Suppose c isthe initial concentration of the salt.

The equilibrium constant, called the *hydrolytic constant* K_h is given by,

$$K_h = \frac{C_{BOH} \cdot C_{H^+}}{C_{B^+}} \qquad \ldots (XXII.10)$$

Now $\quad C_{BOH} = cx, \quad C_{H^+} = cx \quad \text{and} \quad C_{B^+} = c(1-x)$

$$\therefore \quad K_h = \frac{cx.cx}{c(1-x)} = \frac{cx^2}{1-x} \qquad \ldots (XXII.11)$$

That is, degree of hydrolysis x can be evaluated if K_h is known.

When x is quite small, $K_h \approx cx^2$ or $x = \sqrt{K_h/c}$ $\qquad \ldots$ (XXII.12)

The equation (XXII.10) may be written also as

$$K_h = \frac{C_{BOH} \cdot C_{OH^-} . C_{H^+}}{C_{B^+} . C_{OH^-}} = \frac{K_w}{K_b} \qquad \ldots (XXII.13)$$

The concentration of the H^+ ions is cx,

$$\therefore \qquad C_{H^+} = cx = \sqrt{K_h c} \qquad \text{(from equation XXII.12)}$$

or

$$C_{H^+} = \sqrt{\frac{K_w}{K_b} . c}$$

Taking logarithms of the inverse of both sides,

$$pH = \tfrac{1}{2} pK_w - \tfrac{1}{2} pK_b - \tfrac{1}{2} \log c \qquad \ldots (XXII.14)$$

Example 17: The pH of a 0.02 M NH_4Cl solution will be given by,

$$pH = \tfrac{1}{2} \times 14.0 - \tfrac{1}{2}(4.74) - \tfrac{1}{2} \log (2 \times 10^{-2}) = 5.48$$

(for, $K_{NH_4OH} = 1.85 \times 10^{-5}$ or $pK_{NH_4OH} = 4.74$)

$$\therefore \quad x = \frac{C_{H^+}}{c} = \sqrt{\frac{Kw}{K_b c}} = \sqrt{\frac{10^{-14}}{1.85 \times 10^{-5} \times 0.02}} = 5 \times 10^{-3}$$

(*b*) **Salts of Weak Acid and Strong Base.** The hydrolytic equation may be represented as (base being assumed fully ionised as the salt),

$$B^+ + A^- + H_2O \rightleftharpoons BOH + HA = B^+ + OH^- + HA$$

or $\qquad A^- + H_2O \rightleftharpoons OH^- + HA$

Hence the hydrolytic constant (K_h) is given by

$$K_h = \frac{C_{OH^-}.C_{HA}}{C_{A^-}} \qquad \ldots (XXII.15)$$

If c be the orginal concentration of salt and if x be the degree of hydrolysis, then

$$C_{OH^-} = cx, \quad C_{HA} = cx, \quad C_{A^-} = c(1-x)$$

Hence, $$K_h = \frac{cx.cx}{c(1-x)} = \frac{x^2c}{1-x} \qquad \ldots (XXII.16)$$

When x is small, $K_h = x^2c$, hence $x = \sqrt{K_h/c}$ ...(XXII.17)

Again, $$K_h = \frac{C_{OH^-}.C_{HA}}{C_{A^-}} = \frac{C_{OH^-}.C_{HA}.C_{H^+}}{C_{A^-}.C_{H^+}} = \frac{K_w}{K_a} \qquad \ldots (XXII.18)$$

$\therefore$ degree of hydrolysis, $$x = \sqrt{\frac{K_w}{K_a c}} \qquad \ldots (XXII.19)$$

and conc. of OH⁻ ions, $$C_{OH^-} = cx = \sqrt{\frac{K_w.c}{K_a}}$$

$$\therefore \qquad C_{H^+} = \frac{K_w}{C_{OH^-}} = \sqrt{\frac{K_w.K_a}{c}}$$

Taking the negatives of logarithms on both sides,

$$\text{pH} = \tfrac{1}{2}\text{p}K_w + \tfrac{1}{2}\text{p}K_a + \tfrac{1}{2}\log c \qquad \ldots (XXII.20$$

Example 18: The pH of a sodium acetate solution ($0.01M$) is given by,

$$\text{pH} = \tfrac{1}{2} \times 14 + \tfrac{1}{2}(4.74) + \tfrac{1}{2}\log 10^{-2}$$
$$= 7 + 2.37 - 1 = 8.37$$

(for, $K_{acetic\ acid} = 1.8 \times 10^{-5}$, *i.e.*, $pK_a = 4.74$)

The hydrolytic constant, $$K_h = \frac{K_w}{K_a} = \frac{1 \times 10^{-14}}{1.8 \times 10^{-5}} = 5.5 \times 10^{-10}$$

and degree of hydrolysis, $$x = \sqrt{\frac{K_h}{c}} = \sqrt{\frac{5.5 \times 10^{-10}}{1 \times 10^{-2}}} = 2.35 \times 10^{-4}$$

(*c*) **Salts of Weak Acid and Weak Base.** In this case the products of hydrolysis are both weak and hence would be almost undissociated. So,

$$B^+ + A^- + H_2O \rightleftharpoons BOH + HA$$

The hydrolytic constant, $$K_h = \frac{C_{BOH} \times C_{HA}}{C_{B^+} \times C_{A^-}} \qquad \ldots (XXII.21)$$

or $$K_h = \frac{C_{BOH}}{C_{B^+}.C_{OH^-}}.\frac{C_{HA}}{C_{A^-}.C_{H^+}}.C_{H^+}.C_{OH^-}$$

i.e., $$K_h = \frac{K_w}{K_a K_b} \qquad \ldots \text{(XXII.22)}$$

If c be the conc. of the salt solution and x the degree of hydrolysis,

$$K_h = \frac{cx \times cx}{c(1-x).c(1-x)} = \left(\frac{x}{1-x}\right)^2 \qquad \ldots \text{(XXII.23)}$$

So, the degree of hydrolysis and the pH of the solution are independent of the concentration. For the weak acid,

$$K_a = \frac{C_{H^+}.C_{A^-}}{C_{HA}} \quad \text{or} \quad C_{H^+} = K_a.\frac{C_{HA}}{C_{A^-}}$$

$$\therefore \quad C_{H^+} = K_a \frac{cx}{c(1-x)} = K_a . \frac{x}{1-x}$$

Applying eqn. (XXII.23) $$C_{H^+} = K_a\sqrt{K_h} = K_a\sqrt{\frac{K_w}{K_a K_b}} = \sqrt{\frac{K_w.K_a}{K_b}}$$

Hence, $$\text{pH} = \tfrac{1}{2}\text{p}K_w + \tfrac{1}{2}\text{p}K_a - \tfrac{1}{2}\text{p}K_b \qquad \ldots \text{(XXII.24)}$$

When the dissociation constants are equal, *i.e.*,
$pK_a = pK_b$; pH = 7.0, the resulting solution is neutral;
when $K_a > K_b$; pH < 7.0, the solution is acidic;
and when $K_a < K_b$; pH > 7.0, the solution is alkaline.
Given

$K_{CH_3COOH} = 1.8 \times 10^{-5}$, $K_{NH_4OH} = 1.8 \times 10^{-5}$, $K_{HCN} = 7.2 \times 10^{-10}$
The pH of ammonium acetate solution; pH = 7.0 + 2.37 − 2.37 = 7.0, *i.e.*, the solution would be practically neutral.

The pH of ammonium cyanide solution; pH = 7.0 + 4.57 − 2.37 = 9.20 *i.e.*, the solution would be alkaline.

22.12. Determination of Hydrolysis Constant, K_h

There are a number of methods for determining the hydrolytic constant (K_h) of salts. Only two methods are mentioned here. Of course, when the dissociation constants of the weak acid or weak base are known, the hydrolytic constant can be easily computed from eqns. (XXII. 13, 18, 22). The degree of hydrolysis will be known from the K_h-values.

(*a*) pH-*determination Method.* When a salt solution undergoes hydrolysis, the degree of hydrolysis is related to the pH of the solution. We have seen, if it is a salt derived from a weak base-strong acid, then, $C_{H^+} = cx$, where x is the degree of hydrolysis. Otherwise, if it be a salt derived from a strong base-weak acid, $C_{OH^-} = cx$, *i.e.*, $C_{H^+} = K_w/cx$.

In practice the salt solution is taken and its pH is determined with the help of a glass electrode. The conc. of H⁺-ion in the solution is known. From this, the degree of hydrolysis x or the hydrolytic constant K_h can be easily computed.

When the salt is formed from a weak acid-weak base, $C_{H^+} = K_a\sqrt{K_h}$. So the dissociation constant of the acid must also be separately determined.

(*b*) *Conductivity Method.* The conductance of a solution of a salt from a weak acid or a weak base is due partly to the ions of the salt and partly to the ions of the acid or the base formed by hydrolysis. Suppose we consider a salt like aniline hydrochloride formed from a weak base. If c be the concentration of the salt solution and x its degree of hydrolysis, then

$$c.\lambda = c(1-x)\lambda_s + cx\lambda_{HA}$$

i.e., total conductance is the sum of conductances of $c(1-x)$ gm-eqv. of unhydrolysed salt and cx gm equivalents of free acid. λ is the apparent equivalent conductance of the salt in solution which is directly measured. The relation above may be transformed as

$$x = \frac{\lambda-\lambda_s}{\lambda_{HA}-\lambda_s} = \frac{\lambda-\lambda_s}{l_{H^+}+l_{A^-}-\lambda_s} \quad \ldots \text{(XXII.25)}$$

The value λ_{HA} may be taken as $(l_{H^+} + l_{A^-})$ *i.e.*, λ_{0HA} at infinite dilution.

For the determination of (λ_s) the conductance of the unhydrolysed salt, excess of free base aniline is added to the salt solution until the hydrolysis is repressed to a negligible amount. Under this condition, assuming the free-base does not materially contribute to the conductivity, λ_s is experimentally found out. Now that λ, λ_s and λ_{HA} are all known, the degree of hydrolysis x is evaluated by equation XXII.25. from which the value of hydrolysis constant (K_h) can be computed.

Example 19. The equivalent conductance of 0.011 solution of aniline hydrochloride is 120 mhos. When the solution is saturated with excess aniline, the equivalent conductance drops to 104 mhos. The equivalent conductance of HCl at the same concentration is 410 mhos. What are the degree of hydrolysis and the hydrolytic constant?

$$\text{Using eqn. (XXII.25), } x = \frac{\lambda-\lambda_s}{\lambda_{HA}-\lambda_s} = \frac{120-104}{410-104} = 0.052$$

$$\therefore \quad K_h = cx^2 = 0.011 \times (0.052)^2 = 3.0 \times 10^{-5}$$

22.13. Neutralisation Indicators

The acid-base or neutralisation indicators are certain organic weak acids or weak bases which exhibit different colours according to the pH of the solution to which they are added.

It is therefore possible to obtain an idea of the pH of a given solution by adding a little of a suitable indicator to the same. Furthermore, if an indicator is present during the progress of titration of an alkali with an acid, the colour change of the indicator reveals the equivalence point of the titration. Most of the indicators have a predominantly 'acid colour' and a predominantly 'alkaline colour' in lower and higher ranges of pH. Different indicators undergo this change in colour from one to the other in different pH-ranges. For a given acid-base titration we can therefore select the indicator which would show a colour change at the equivalence point of that reaction.

Some of the commonly used acid-base indicators with the pH-ranges for their colour-change are listed below:

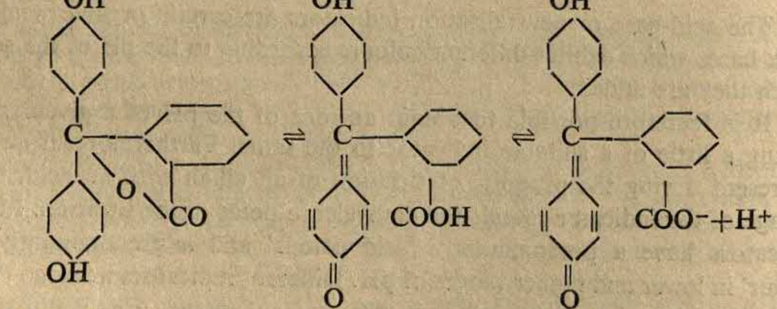
TABLE: ACID-BASE INDICATORS

Indicator	pK_{in}	*Colour-change acid-alkali*	pH-*range*
Bromo-phenol blue	4.0	yellow-blue	2.8– 4.6
Methyl orange	3.7	red-yellow	3.1– 4.4
Bromo cresol-green	4.7	yellow-blue	3.8– 5.4
Methyl red	5.1	red-yellow	4.2– 6.3
Chlorophenol red	6.0	yellow-red	4.8– 6.4
p-nitrophenol	7.1	colourless-yellow	5.6– 7.6
Bromo-cresol purple	6.3	yellow-purple	5.2– 6.8
Bromo-thymol blue	7.0	yellow-blue	6.0– 7.6
Phenol red	7.9	yellow-red	6.8– 8.4
Cresol red (base)	8.3	yellow-red	7.2– 8.8
Thymol blue (base)	8.9	yellow-blue	8.2– 9.6
Phenolphthalein	9.6	colourless-red	8.3–10.0
Thymolphthalein	9.2	colourless-blue	8.3–10.5

Theory of Indicators. The present theory by which the action of the indicators is explained is known as the **Quinonoid Theory**. It assumes that the indicators (acids or bases) exist in two tautomeric forms. One of the tautomers is in the non-electrolytic form and scarcely ionises but the other is an electrolyte and hence ionisable. The colours of the two tautomeric forms are different. The colour of the ion is the same as that of the tautomer from which it is produced.

For example, the commonly used indicator, phenolphthalein exists as follows:

(*a*)



Colourless lactone (Benzenoid form)

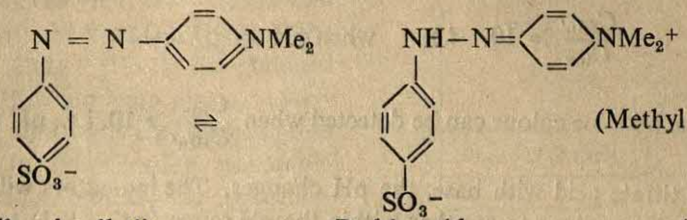
Red (Carboxylic acid)

Red (ionised)

(Quinonoid form)

Methyl orange, another common indicator which is a base, has two tautomeric forms, as,

(b)



(Methyl orange)

Yellow in alkalis   Red in acids   etc.

To illustrate: Let us consider an indicator acid like phenolphthalein. Suppose HIn′ be the non-ionisable tautomeric form and HIn be the ionisable form, while In^- represents the indicator ion. The colour of HIn and In^- is the same but different from that of HIn′. In aqueous solution there would exist two equilibria.

$$(i)\ \mathrm{HIn'} \rightleftharpoons \mathrm{HIn} \quad \ldots.\ K_t = \frac{C_{\mathrm{HIn}}}{C_{\mathrm{HIn'}}} \quad \ldots(\mathrm{A})$$

$$(ii)\ \mathrm{HIn} \rightleftharpoons \mathrm{H^+} + \mathrm{In^-} \quad \ldots.\ K_D = \frac{C_{\mathrm{H^+}}.C_{\mathrm{In^-}}}{C_{\mathrm{HIn}}} \quad \ldots(\mathrm{B})$$

In acid solutions, the dissociation will be repressed, the whole of the indicator shall remain in undissociated form *i.e.*, as HIn′ and HIn, which have different colours. The indicators will be applicable only if the equilibrium constant K_t of equation (A) is small, so that the undissociated indicator mostly exist as HIn′.

$$\text{Multiplying (A) and (B),}\quad \frac{C_{\mathrm{H^+}}C_{\mathrm{In^-}}}{C_{\mathrm{HIn'}}} = K_t.K_D = K_{in}\ \text{(say)} \quad \ldots(\mathrm{C})$$

where K_{in} is called the 'indicator constant'.

It has been assumed that the conc. of HIn is very small. Therefore $C_{\mathrm{HIn'}}$ is the conc. of practically the entire undissociated form. The colour of HIn′ is the colour which the indicator will show in *acid* medium.

In presence of alkali, H^+ ions will be removed as H_2O, dissociation will be almost complete and the indicator will be present mostly as In^-. Hence indicator ion shall have 'alkali' colour.

$$\text{Rewriting (C),}\quad C_{\mathrm{H^+}} = K_{in}\,.\,\frac{C_{\mathrm{HIn'}}}{C_{\mathrm{In^-}}} \quad \ldots(\mathrm{D})$$

$$\text{Hence,}\quad \mathrm{pH} = \mathrm{p}K_{in} + \log\frac{C_{\mathrm{In^-}}}{C_{\mathrm{HIn'}}} \quad \ldots(\mathrm{XXII.26})$$

$$\text{or}\quad \mathrm{pH} = \mathrm{p}K_{in} + \log\frac{C_{\textit{ionised form with alkaline colour}}}{C_{\textit{non-ionised form with acid colour}}}$$

At any given pH, indicator exists in a definite ratio of concentrations of ionised and non-ionised form. But human eye can discern the colour distinctly when one predominates. It has been found that the acid colour, namely that of HIn′, is detected when

$$\frac{C_{\text{HIn}'}}{C_{\text{In}^-}} \geqslant 10, \quad i.e., \quad \text{when pH} = \text{p}K_{in}-1.$$

And the alkaline colour can be detected when $\frac{C_{\text{In}^-}}{C_{\text{HIn}'}} \geqslant 10$, i.e., $\text{pH} = \text{p}K_{in}+1$.

As we titrate acid with base, the pH changes. The indicators will appear to change from one colour to another within the pH range ($\text{p}K_{in}+1$) to ($\text{p}K_{in}-1$), within two units of pH.

Thus, phenolphthalein has a $\text{p}K_{in}$ value of 9.6 and hence its colour change takes place in the pH range 8.6 to 10.6. Methyl red has a $\text{p}K_{in}$ value of 5.1, so its colour would change in the pH-range 4.1 to 6.1.

Choice of Indicators. When equivalent amounts of a strong acid (say HCl) and a strong base (say KOH) are mixed, the resultnig solution has a pH near about 7.0 and any indicator may be used in such neutralisation titrations. On the other hand, if to a weak acid solution an equivalent amount of a strong base be added, the resulting salt in solution suffers hydrolysis and the solution is alkaline having a pH above 7.0. Hence in a titration of a weak acid and a strong base, indicators whose colour-change takes place in a higher range, such as phenolphthalein or thymol-blue should be used. In titrating a strong acid with a weak-base (say HCl acid with Na_2CO_3 soln), the resulting salt suffers hydrolysis and the solution becomes acidic even when equivalent amounts are added. The indicators like methyl orange, methyl red etc. whose colour-change takes place in the acidic pH-range would prove satisfactory. In titration of weak acids with weak bases, none of the indicators are very satisfactory.

The satement just made may be more clearly understood from a titration curve with variation in pH of the solution.

Suppose 25 c.c. of 0.1*N* HCl are being titrated with 0.1*N* NaOH. Assuming complete dissociation the H^+-ion concentration at any stage of titration is equal to the amount of HCl remaining unneutralised. The pH-values may then be calculated as:

c.c. of NaOH added	% HCl unneutralised	C_{H^+}	pH
0	100	10^{-1}	1.0
12.5	50	3.3×10^{-2}	1.48
24.9	0.4	2×10^{-4}	3.70
25.0	0.0	10^{-7}	7.00
25.1	alkaline	5×10^{-11}	10.30

This shows that when only 0.1 c.c. of titre remains to be added to reach equivalence point. pH was 3.70. On addition of another 0.2 c.c. titre, the pH jumps sharply to 10. This is clearly illustrated in Fig. XXII.1 (II–I). The point where sudden rise occurs is the equivalence point.

If instead of HCl, 0.1N acetic acid is titrated with 0.1N NaOH the titration curve Fig. XXII.1 (IV–I) is obtained where the pH would jump approximately from 7.0 to 10.0 when equivalence point is reached. In this titration, phenolphthalein is used as indicator as its colour-change occurs at about pH = 9.0.

In titrating 0.1N HCl with 0.1N NH_4OH solution, the pH-changes calculated with Henderson equation, shows a steep rise from 4.0 to 7.0 when equivalence point is reached as in Fig. XXII.1 (II-III). Melthyl Orange would be a suitable indicator in this range.

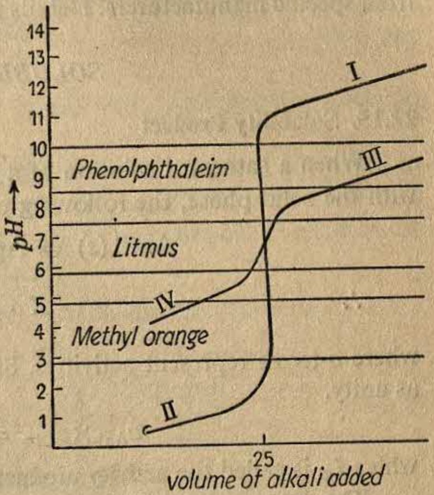


Fig. XXII.1
Acid base neutralisation curves

(*a*) II-I → HCl titrated with NaOH
(*b*) II-III → HCl titrated with NH_4OH
(*c*) IV-I → CH_3COOH titrated with NaOH
(*d*) IV-III→ CH_3COOH titrated with NH_4OH

22.14. Determination of pH of a Solution by Colorimetric Method

The first step is to have an idea of the approximate pH of the given solution. This is done with the help of a universal multirange B.D.H. indicator. This is indeed a mixture of several indicators. The B.D.H. universal indicator when added to the solution develops a colour which is matched against colour charts supplied by the manufacturers. This enables one to have an approximate estimate of the pH-range of the solution under test.

Suppose the approximate pH of the solution is found to be in the range 6.0—7.0. A series of buffer solutions are then prepared in that range, say from pH = 5.0 to pH = 7.6 differing successively in pH by about 0.2. In this case, primary-secondary phosphate buffers will be suitable. Ten c.c. of each of these buffer solutions are taken in clean test tubes and to each 0.5 c.c. of an indicator soln suitable for that pH-range is added [here Bromothymol blue (B.T.B.) indicator would be suitable]. The buffer solutions will have gradually changing shades of colour. In another test tube of same dimensions, 10 c.c. of the experimental solution is taken to which 0.5 c.c. of the same indicator is added. The colour produced is then compared with the coloured buffer solutions. When a complete match is obtained, the test solution and the corresponding buffer solution will have the same pH. In this way, pH-value of the solution accurate up to 0.2 pH unit can be determined. A more accurate value can be obtained if buffers could be prepared differing by 0.1 pH unit. Often Lovibond or Hellige comparator is used for matching the colours. Series of permanent glass colour standards for different pH-ranges are supplied, fitted in a disc. Solutions with indicators are taken in small rectangular cells and matched with the coloured glass standards to obtain the pH-value. Indicators to be used for such comparator methods are also to be obtained from specific manufacturers. Details may be found in a practical text book.

SOLUBILITY PRODUCT

22.15. Solubility Product

When a saturated solution of a *sparingly soluble salt*, say AgCl, is in contact with the solid phase, the following equilibria exist.

$$\text{AgCl}\,(s) \rightleftharpoons \text{AgCl}\,(soln) \rightleftharpoons \text{Ag}^+ + \text{Cl}^-$$

$$\therefore \qquad K = \frac{a_{\text{Ag}^+} \times a_{\text{Cl}^-}}{a_{\text{AgCl}(s)}},$$

where a-terms represent activities. Since the activity of the solid phase is taken as unity.

$$a_{\text{Ag}^+} \times a_{\text{Cl}^-} = K.a_{\text{AgCl}(s)} = L_a$$

where L_a is called the **activity product** of the salt at a given temperature.

The saturated solution being extremely dilute, activity may be taken to be equal to concentrations for ordinary purposes except where great accuracy is required.

$$\therefore \qquad C_{\text{Ag}^+} \times C_{\text{Cl}^-} = L_S$$

L_S is the **solubility product.**

The solubility product is defined as the product of the ionic concentrations in a saturated solution of a sparingly soluble salt and is a constant quantity at a given temperature.

When the salt ionises into different numbers of cations and anions, the concentrations are to be raised to powers equal to the number of ions produced. For a salt like $Ca_3(PO_4)_2$ in saturated solution,

$$Ca_3(PO_4)_2 \rightleftharpoons 3Ca^{++} + 2\,(PO_4)^{---}$$

$$L_S = C^3_{Ca^{++}} \times C^2_{PO_4^{---}}$$

In general, for a salt A B_q, $L_S = C_A^p \times C_B^q$ ... (XXII.27)

22.16. Solubility Product and Solubility

Suppose S is the solubility of a sparingly soluble salt (AgCl, say) expressed in *gm-moles per litre*. Assuming complete dissociation in the dilute solution,

$$C_{\text{Ag}^+} = S \ ; \ C_{\text{Cl}^-} = S \ ; \text{ hence } L_S = S^2$$

$$\therefore \text{ Solubility, } S = \sqrt{L_S}$$

Again, for the solubility (S) of $Ca_3\,(PO_4)_2$,

$$C_{Ca^{++}} = 3S, \ C_{PO_4^{---}} = 2S \ ; \text{ hence } L_S = (3S)^3 \times (2S)^2 = 108S^5$$

$$\therefore \qquad \text{Solubility, } S = \left(\frac{L_S}{108}\right)^{\frac{1}{5}}$$

In general, if s be the solubility of a sparingly soluble salt, A_pB_q then

$$C_{A+} = ps, C_{B-} = qs; \quad L_S = C^p{}_{A+}.C^q{}_{B-} = (ps)^p.(qs)^q$$

or
$$S = \left(\frac{L_S}{p^p q^q}\right)^{\frac{1}{p+q}} \qquad \ldots (XXII.28)$$

The presence of an ion common with one of the ions of the sparingly soluble salt lowers the solubility of the latter.

It is easily seen that if to a saturated solution of a sparingly soluble salt is added a compound containing a common ion the former will be thrown out of solution. If S be the solubility of AgCl in pure water and suppose x gm-eqv. of KCl be added to a litre of the saturated solution.

$$L_s = C_{Ag+}.C_{Cl-} = S'(S'+x); \quad S' \text{ is the new solubility.}$$

But
$$L_s = S^2; \quad \text{or} \quad S'(S'+x) = S^2$$

i.e.,
$$S' = -\frac{x}{2} + \sqrt{\frac{x^2}{4} + S^2} = -\frac{x}{2} + \sqrt{\frac{x^2}{4} + L_s}$$

The new solubility can thus be predicted. S' is less than S.

Example 20. Calculate the solubility product of silver chromate if its solubility be 2.5×10^{-2} gm per litre.

Also find out its solubility in $0.001M$ potassium chromate solution. The activity coefficients may be taken as unity.

(*a*) Solubility of $Ag_2CrO_4 = \dfrac{2.5 \times 10^{-2}}{332} = 7.5 \times 10^{-5}$ mol/litre.

(mol. wt. = 332)

Assuming complete dissociation,

$$C_{Ag+} = 2 \times 7.5 \times 10^{-5} \qquad C_{CrO_4--} = 7.5 \times 10^{-5}$$

The solubility product, $L_s = C^2{}_{Ag+}.C_{CrO_4--} = (2 \times 7.5 \times 10^{-5})^2(7.5 \times 10^{-5})$
$= 1.7 \times 10^{-12}$

(*b*) The conc. of Ag^+ in saturated solution, in presence of pot. chromate,

$$C_{Ag+} = \left(\frac{L_s}{C_{CrO_4--}}\right)^{\frac{1}{2}} = \left(\frac{1.7 \times 10^{-12}}{1 \times 10^{-3}}\right)^{\frac{1}{2}} = 4.1 \times 10^{-5} \text{ moles/litre}$$

Hence the solubility is 2.05×10^{-5} moles/litre.

The decrease in solubility by common ion effect is of considerable importance in gravimetric analysis. Suppose silver is precipitated from a solution by potassium chromate. If exactly equivalent amount of chromate be added, the amount of silver that would remain in solution (see problem above) is 1.5×10^{-4} moles/litre. But if we use excess potassium chromate until its conc. is $0.001M$, the loss will be reduced to 4.1×10^{-5} moles/litre. That is why the precipitant is to be added in excess.

When the addition of a common ion or an inert salt leads to a considerable increase in the solubility of a salt it may be reasonably concluded that a complex ion has been formed. This happens when say NH_4Cl is added to saturated AgCl solution or KI solution is added to HgI_2 solution, etc.

22.17. Determination of the Solubility Product

(*a*) It has been seen in Sec. 20.20 that the solubility of a sparingly soluble salt can be accurately determined from conductance measurement. With the knowledge of solubility, the solubility product can be computed with eqn. XXII.28.

In Sec. 21.11, we have seen the determination of solubility product from concentration cells.

(*b*) The solubility product or the more accurate 'activity product' can be obtained also from emf measurement of suitably constructed cells.

To illustrate: let us take the case of AgCl. In a solution of 0.1*M* KCl ($f_\pm = 0.77$) is added a few drops of $AgNO_3$, so that the solution is saturated with AgCl, and a silver wire is inserted in the solution. This can serve as a silver electrode, Ag/Ag^+. This electrode is coupled with a 0.1*N* calomel electrode. The emf of the cell is measured and found at 25°C to be 0.0494 volts.

$$\mathrm{Ag} \left| \begin{array}{l} \mathrm{0.1N\ KCl} \\ \text{saturated with AgCl} \end{array} \right\| \mathrm{Hg_2Cl_2} \,|\, \mathrm{Hg}; \quad E = 0.0494$$

The emf, $E = \xi_{Ag} - \xi_{calomel}$

or $0.0494 = \xi_{Ag} + 0.3338,$

whence, $\xi_{Ag} = -0.2844$ volts

But $\xi_{Ag} = \xi^{\circ}_{Ag} - 0.059 \log a_{Ag^+},$ where $\xi^{\circ}_{Ag} = -0.799$

or $\log a_{Ag^+} = -\dfrac{0.799-0.2844}{0.059}$

whence $a_{Ag^+} = 2 \times 10^{-9}$

The activity of Cl^- ions in the solution is $0.1 \times 0.77 = 0.077$

Hence, the activity product, $L_a = a_{Ag^+} \times a_{Cl^-}$

$$= 2 \times 10^{-9} \times 0.077 = 1.54 \times 10^{-10}$$

In the table appended below are given the solubility products of some common sparingly soluble compounds and salts at room temperature:

Substance	L_S
AgCl	1.5×10^{-10}
AgBr	7.7×10^{-13}
AgI	0.9×10^{-16}
Ag_2CrO_4	2.5×10^{-12}
$BaSO_4$	9.2×10^{-11}
$CaSO_4$	2.3×10^{-4}
$SrSO_4$	2.8×10^{-7}
$PbCl_2$	2.4×10^{-4}
$PbBr_2$	7.9×10^{-5}
PbI_2	8.7×10^{-9}
$CaCO_3$	4.8×10^{-9}
CaOx	2.6×10^{-9}
CaF_2	3.2×10^{-11}
CuCl	1×10^{-6}
CuBr	1.6×10^{-11}
CuI	5×10^{-12}
$Fe(OH)_3$	1×10^{-38}
$Al(OH)_3$	1×10^{-33}
$Cr(OH)_3$	1×10^{-30}
$Zn(OH)_2$	1×10^{-17}
$Co(OH)_2$	2×10^{-16}
$Ni(OH)_2$	1×10^{-14}
$Mg(OH)_2$	6×10^{-12}
HgS	3×10^{-54}
CuS	3×10^{-42}
CdS	4×10^{-29}
PbS	4×10^{-28}
CoS	2×10^{-27}
ZnS	1×10^{-23}
NiS	1.4×10^{-24}
MnS	2×10^{-15}

22.18. Applications of Solubility Product measurement

The measurement of solubility product has various applications, especially in the field of chemical analysis. It helps in the determination of composition of complex salt, in the determination of activity coefficients, in the determination of some equilibrium etc.

Determination of equilibrium between two poorly soluble salts. Let us consider the reaction:

$$AgCl(s) + I^- = AgI(s) + Cl^-$$

The eqm. constant, $K_c = \dfrac{C_{Cl^-}}{C_{I^-}} = \dfrac{C_{Ag^+} . C_{Cl^-}}{C_{Ag^+} . C_{I^-}} = \dfrac{L_{s(AgCl)}}{L_{s(AgI)}}$

Substituting the experimental values $L_{s(AgCl)} = 1.5 \times 10^{-10}$ and $L_{s(AgI)} = 1 \times 10^{-16}$, $K_c \approx 1.5 \times 10^6$. Hence the reaction will proceed to the right even when C_{I^-} is one-millionth of that of C_{Cl^-}. So a poorly soluble salt displaces a more soluble one from a precipitate.

Solubility Product and Analysis: The routine analytical scheme of inorganic samples is based on the operation of discriminatory dissolution and precipitation of the components of a mixture with the help of suitable reagents. These are always governed by the principle of solubility product.

(*a*) *Solubility of Sparingly Soluble Salts of Weak Acids in Strong Acids.* There are many salts of weak acids, such as $Ca_3(PO_4)_2$, which are insoluble in water but are taken into solution with HCl.

$$Ca_3(PO_4)_2 + 6HCl \rightarrow 3CaCl_2 + 2H_3PO_4$$

In a saturated solution in water, $C^3_{Ca^{++}} \times C^2_{PO_4^{---}} = L_s$

the solubility product is low and hence solubility is quite small. Addition of a strong acid. *i.e.*, H^+ ions, reduces the phosphate ion concentration by forming undissociated phosphoric acid, as

$$(PO_4)^{---} + 3H^+ \rightarrow H_3PO_4$$

The decrease in the concentration of PO_4^{---} ions enables more calcium phosphate to go into solution to maintain the constancy of L_s. The addition of Cl^- ions along with H^+ -ions do not affect, for $CaCl_2$ salt is highly soluble and practically fully ionised.

(*b*) *Precipitation from a Solution.* This indeed is the most important operation in analysis to separate out a component. The solubility product is the limiting value of the product of ionic concentrations $(C_+)^m.(C_-)^n$ in the saturated state when solid phase is in equilibrium with the ions in solution. When the experimental conditions are arbitrarily so manipulated that the ionic concentration product exceeds the solubility product, the law demands that some ions must be removed. This is achieved by the system with the formation of solid phase, which is the precipitate. Thus to a barium nitrate solution if ammonium sulphate is added, the ionic concentration product $C_{Ba^{++}}.C_{SO_4^{--}}$ almost immediately exceeds L_{BaSO_4}, which is very low (9.2×10^{-11}). Hence, the ions combine together to form the insoluble barium sulphate to be precipitated. The sulphate ions are therefore good precipitating agents for Ba^{++}. This is the story of other precipitations usually met with in the analytical scheme.

(*c*) *Precipitation of Sulphides.* It is common knowledge that basic radicals like those of Hg, Cu, Pb, etc. are precipitated as sulphides in acid solution in Group II and those of Ni, Mn, etc. are precipitated in alkaline media in Group III*b*. It may be remembered that the sulphides of the former category (Hg, Cu, etc.) have very low solubility products compared to those of the later category (Zn, Mn, Ni, etc.)

Sulphides	L_s	*Sulphides*	L_s
HgS	3×10^{-54}	MnS	2×10^{-15}
CuS	3×10^{-42}	NiS	1.4×10^{-25}
PbS	4×10^{-28}	ZnS	1×10^{-23}

When H_2S is passed into solutions containing these radicals there arises the question of equilibrium between metal ions and the sulphide ions. As soon as the ionic concentration product exceeds the corresponding solubility product, the sulphide is precipitated.

It must be realised that the concentration of sulphide ion depends on the H^+ ion concentration in the solution, for

$$H_2S \rightleftharpoons 2H^+ + S^{--}; \qquad K_{H_2S} = C^2_{H^+} \times C_{S^{--}} / C_{H_2S}$$

Hence,
$$C_{S^{--}} = \frac{K_{H_2S} \times C_{H_2S}}{C^2_{H^+}}$$

where C_{H_2S} may be taken as the solubility of H_2S in water, which is about M/10 *i.e.*, 10^{-1}. The concentration of sulphide ion is inversely proportional to the square of the H^+ ion concentration. So, in acid solutions $C_{S^{--}}$ will be low and only those sulphides whose solubility product is very low shall be precipitated.

The magnitude of $K_{H_2S} = 1 \times 10^{-22}$

$$\therefore \qquad C_{S^{--}} = \frac{1 \times 10^{-22} \times 10^{-1}}{C^2_{H^+}} = \frac{1 \times 10^{-23}}{C^2_{H^+}}.$$

Suppose in a normal hydrochloric acid solution we have Cu^{++} and Mn^{++} ions present whose approximate concentrations are M/10. Then in this solution if H_2S is passed, the concentration of sulphide ions, $C_{S^{--}} = \frac{1 \times 10^{-23}}{1^2} = 1 \times 10^{-23}$.

Then, the ionic product of $Cu^{++}$and S^{--}ions $= (1 \times 10^{-1})(1 \times 10^{-23}) = 1 \times 10^{-24}$ which is much larger than L_{CuS} and hence CuS will be precipitated in acid solution. But this value is much smaller than L_{MnS} and hence MnS will not be precipated.

In alkaline solution, say with $C_{H^+} = 10^{-8}$, the sulphide ion concentration is $C_{S^{--}} = \frac{1 \times 10^{-23}}{10^{-16}} = 1 \times 10^{-7}$.

$$\therefore \text{ ionic product } C_{Mn^{++}} \times C_{S^{--}} = (1 \times 10^{-1})(1 \times 10^{-7}) = 1 \times 10^{-8}$$

Since this exceeds L_{MnS}, in alkaline medium manganese sulphide shall be precipitated.

The precipitation of Fe, Al, etc. as hydroxides is also explained in the same way.

(*d*) *Use of K_2CrO_4 as Indicator.* In the estimation of a chloride by titration with silver nitrate solution, K_2CrO_4 solution is added to act as an indicator. Advantage is taken of the difference in the solubility products of silver chloride the silver chromate.

$$L_{AgCl} = C_{Ag^+}.C_{Cl^-} = 1 \times 10^{-10}$$

$$L_{Ag_2CrO_4} = C^2_{Ag^+}.C_{CrO_4^{--}} = 2.5 \times 10^{-12}$$

In titration, say a (N/10) NaCl solution with a (N/10) $AgNO_3$ solution, potassium chromate is added such that its strength is approximately M/100. That is, at the beginning $C_{Cl^-} = 10^{-1}$, $C_{CrO_4^{--}} = 10^{-2}$.

When initially just a little $AgNO_3$ solution is added, say $C_{Ag^+} = 10^{-10}$ then ionic products will be,

$C_{Ag^+}.C_{Cl^-} = 10^{-10} \times 10^{-1} = 10^{-11}$; $C^2_{Ag^+}.\ C_{CrO_4^{--}} = (10^{-10})^2 \times 10^{-2} = 10^{-22}$ These quantitities are less than the solubility products of both and hence no ppt. will come out.

On further addition of $AgNO_3$, say $C_{Ag^+} = 10^{-8}$, we have $C_{Ag^+}.C_{Cl^-} = 10^{-9}$, $C^2_{Ag^+}.C_{CrO_4^{--}} = 10^{-18}$. It is evident AgCl will be precipitated but not Ag_2CrO_4.

When precipitation of silver chloride is just complete, the conc. of $Ag^+ = 10^{-5}$. Therefore, $C^2_{Ag^+}.C_{CrO_4^{--}} = 10^{-12}$. On addition of just a little more $AgNO_3$ the conc. of Ag^+ will be large enough to cause ionic product $C^2_{Ag^+}.C_{CrO_4^{--}}$ exceed $L_{Ag_2CrO_4}$ ($= 2.5 \times 10^{-12}$) and hence Ag_2CrO_4 will begin to precipitate with its typical colour and the end point is known from the colour-change. Sufficient potassium chromate is to be used as indicator so as to produce enough silver chromate to saturate the solution and be precipitated.

EXERCISES

1. What is meant by ionisation constant of an acid?

At 20°C, a 0.1*N* formic acid solution dissociates to an extent of 4.5%. Calculate its ionisation constant. [Ans. 2.1×10^{-4}]

2. At 30°C, *N*/10 solution of propionic acid dissociates to an extent of 1.13%. To what extent will this acid be dissociated in a 0.01 *N* solution? [Ans. 9.6%]

3. Discuss Ostwald's dilution law and point out its significance.

The equivalent conductance of *N*/16 solution of acetic acid is 6.1 and the conductance at infinite dilution is 364 mhos. Find out the dissociation constant of the acid. [Ans. 1.78×10^{-5}]

4. What do you understand by pH of a solution? Calculate approximately the pH of aqueous solutions of 0.01 *M* HCl and 0.02 *M* NaOH. [Ans. 2.0; 12.3]

5. Using K_a or K_b values from the table, find out the pH of the following solutions: (*i*) 0.01 *N* HCN (*ii*) 0.05 *M* acetic acid (*iii*) 0.05 *M* NH_4OH

6. What will be the H^+ ion concentrations of solutions having (*i*) pH = 4.5 (*ii*) pH = 8.4?

7. Find out the pH of a 0.02 *N* weak acid solution if it be 5.0% dissociated in this solution. [Ans. 2.7]

8. Calculate pH of solutions having hydrogen ion concentrations (*i*) 5×10^{-3} (*ii*) 2×10^{-6} gm-eqv./litre [Ans. (*i*) 2.3 (*ii*) 5.7]

9. What will be the pH of a solution obtained by mixing 800 c.c. of 0.05 *N* NaOH and 200 c.c. of 0.1 *N* HCl assuming complete dissociation for both. (Guru Nanak B.Sc. '75) [Ans. 12.3]

10. (*a*) A 0.1 molar solution of a monobasic acid dissociates to an extent of 1%. Calculate ionisation constant of the acid.

(*b*) Calculate the H^+-ion concentration of 0.1 *M* HCN solution if the dissociation constant of the acid is 7.2×10^{-10} at 25°C. (Bangalore Univ.) [Ans. (*a*) 1×10^{-5} (*b*) 8.5×10^{-6}]

11. Calculate the H^+-ion concentration of 0.1 *M* acetic acid. The value of K_a is 1.752×10^{-5}. (Delhi Univ.) [Ans. 1.32×10^{-3}]

12. The molecular conductivity of a weak monobasic acid at infinite dilution is 387 ohm^{-1}. The specific conductivity of the same acid at a dilution of *N*/50 is 0.00033. at the same temperature. What is the percentage dissociation of the acid in *N*/50 dilution? (Agra Univ. '72). [Ans. 4.27%]

13. The specific conductivity of a 0.1 *N* acetic acid is 0.000471 *r.o.* and that of 0.001 *N* sodium acetate solution is 0.0000781 *r.o.* What is the dissociation constant of the acid at 18°C if the ionic conductivity of H^+ ion is 318 and that of sodium ion is 44.4 and if the sodium acetate solution is regarded as completely ionised? (Delhi Univ. '70) [Ans. 1.8×10^{-5}]

14. The dissociation constants of acetic acid and formic acid are 1.8×10^{-5} and 2.1×10^{-4} respectively. Calculate the relative strength of formic acid compared to acetic acid. [Lucknow Univ. '72] [Ans. (3.4 : 1)]

15. A solution which is 0.05 *M* in respect of benzoic acid and 0.01 *M* solution in respect of sodium benzoate has a pH = 4.50. Find the dissociation constant of the acid. [Ans. 6.3×10^{-5}[

16. Calculate the ionic product of water from the e.m.f. of the following cell at 25°C: (Pt)-H_2 (1 atm) | KOH(0.01 *m*) || KCl (0.01 *m*) | AgCl(*s*) | Ag; e.m.f. = 1.0503 volts.

17. At 10°C, the ionic product of water is 0.314×10^{-14} and at 34°C it is 2.16×10^{-14}. Calculate the heat of formation of water from H^+ and OH^- ions. [C. U. 1976]

18. 10 c.c. of a 0.1 *M* NaOH solution are added to 50 c.c. of a 1.1 *M* acetic acid solution. What will be the pH of the resulting solution? $K_{HAC} = 1.75 \times 10^{-5}$. [C. U. 1977]

19. Calculate pH of solutions:

(*i*) 0.05 molal lactic acid and 0.122 molal Na-lactate ($K_a = 1.37 \times 10^{-4}$)

(*ii*) 0.1 molal NH_4OH and 0.24 molal NH_4Cl ($K_b = 1.8 \times 10^{-5}$).

20. Calculate the pH of a solution of 0.1 *N* acetic acid given $K_{HAc} = 1.85 \times 10^{-5}$ at room temperature. What is the effect of dissolving 0.1 mole of sodium acetate in one litre of the acid solution? (Sri Venkataswara Univ. '73). [Ans. 2.87; pH becomes 4.73]

21. Calculate pH of a solution containing 0.18 mole of acetic acid and 0.18 mole of sodium acetate per litre at 25°C. The ionisation constant of acetic acid at 25°C is 1.8×10^{-5}. (Saurashtra Univ. '71) [Ans. 4.74]

22. What is the pH of a buffer solution of 0.1 *M* HCN in 0.1 *M* KCN? The dissociation constant of HCN = 4×10^{-10}. (Shivaji Univ. '70) [Ans. 9.4]

23. A buffer solution containing 0.2 mole of acetic acid and 0.02 mole of sodium acetate per litre is found to have a pH = 3.757. If to this solution 1 c.c. of 0.01 *N* HCl be added what would be the pH of the resulting liquid. ($K_a = 1.752 \times 10^{-5}$). (Agra Univ. '72) [Ans. 3.755]

24. Calculate the percentage hydrolysis of sodium acetate in 0.1 *N* solution at 25°C. [$K_a = 1.8 \times 10^{-5}$] (C. U. 1975) [Ans. 7.5×10^{-3}]

25. Calculate (using standard values of dissociation constants),

(*a*) the degree of hydrolysis of (*i*) 0.01 molar and 0.001 molar Na_2CO_3 solutions and (*ii*) 0.1 molar KCN solution at 25°C.

(*b*) the hydrolytic constants of (*i*) ammonium carbonate and (*ii*) disodium hydrogen phosphate.

26. At 25°C and at a dilution of 32 litres, the eqv. conductance of ortho-toluidine hydrochloride is 98.5 and that of HCl at the same concentration is 383. On adding successive quantities of orthotoluidine to the solution of the salt, the eqv. conductance could be reduced to 89.7 but no further. Find out the degree of hydrolysis and the hydrolytic constant.

27. A solution of 12.95 gm of aniline hydrochloride in 100 c.c. of 0.01 *N* HCl is brought into equilibrium with 100 c.c. of benzene. The amount of aniline in benzene layer was estimated to be 0.1 gm. What is the hydrolysis constant of aniline hydrochloride, if partition coefficient of aniline between benzene and water is 10.

28. Calculate the percentage of hydrolysis of *N*/10 sodium acetate solution at 25°C. K_a is 1.8×10^{-5} and $K_w = 1.01 \times 10^{-14}$ at the same temperature (Bangalore Univ. '74).
[Ans. 0.0075%]

29. At 25°C, the ionic product of water is 1×10^{-14} and dissociation constant of acetic acid is 1.8×10^{-5}. Calculate hydrolysis constant of sodium acetate. What is the degree of hydrolysis in 0.01 *N* solution? (Agra Univ. '71) [Ans. 5.56×10^{-10}; 2.36×10^{-4}]

30. Explain the conductivity method to determine the degree of hydrolysis of aniline hydrochloride.

Determine the hydrolysis constant, degree of hydrolysis and pH of 0.1 *M* ammonium acetate given that

$K_a = 1.752 \times 10^{-5}$, $K_w = 1 \times 10^{-14}$ and $K_b = 1.74 \times 10^{-5}$. (Shivaji Univ. '71)
[Ans. 3.28×10^{-5}; 0.573% ; 6.998]

31. An aqueous solution of NH_4Cl is acidic. Explain.

Calculate the pH of a decinormal solution of NH_4Cl.

$pK_b = 5.7$; $pK_w = 14$, at the same temperature. (Utkal Univ. '70) [Ans. 4.65]

32. Justify the use of indicators mentioned below in following titrations at 25°C:

(*i*) Methyl red ($pK_{in} = 5.1$) in the titration of NH_4OH($K_b = 1.74 \times 10^{-5}$) with HCl soln.

(*ii*) Phenophthalein ($pK_{in} = 9.4$) in the titration of benzoic acid ($K_a = 6.3 \times 10^{-5}$) with NaOH soln. [C. U. 1968]

33. The solubility of AgCl in water is 1.50 mgm/litre at 20°C. What will be its solubility in 1×10^{-3} *M* KCl solution?

34. The solubility product of Magnesium hydroxide is 1.8×10^{-11}. Calculate its solubility in gm/litre. (Gauhati Univ. '73) [Ans. 9.57×10^{-3} gm/litre]

35. At 25°C, the solubility product of $AgBrO_3$ is 5.8×10^{-5}. Calculate its solubility in pure water and in 0.01 *M* $KBrO_3$.

36. The solubility product of PbI_2 is 7.5×10^{-9} at 15°C and 1.4×10^{-8} at 25°C. Show that the molar heat of solution of PbI_2 is 10,600 calories. Calculate the solubility of PbI_2 at 35°C.

37. At 25°C the activity product $L_a = 7 \times 10^{-9}$ for MgF_2. Calculate its solubility in moles/litre in water and in 0.01 *M* NaF. [Ans. 1.2×10^{-3}, 7×10^{-5}]

38. At 18°C, the specific conductance of water saturated with CaF_2 is 3.86×10^{-5}. Show that its solubility is 1.48×10^{-2} gm/litre. Calculate its solubility product.

Given $l_+ = 51$, $l_- = 47$, and the specific conductance of water used, 1.5×10^{-6}.

39. The e.m.f. of the cell

Calomel electrode (saturated) | KCl | AgCl(*s*) | Ag

was found to be 0.269 volts at 25°C. What is the solubility of silver chloride? (Given $\mathcal{E}^0_{Cal} = 0.2415$ and $\mathcal{E}^0_{Ag/Ag^+} = 0.7978$ volts).

40. For $AgCl(s) \rightleftharpoons Ag^+ + Cl^-$; $\Delta H^\circ = 15650$ cal. Given $S^\circ_{AgCl} = 22.97$, $S^\circ_{Ag^+} = 17.67$, $S^\circ_{Cl^-} = 13.17$ e.u. Calculate the solubility product of AgCl at 25°C. [Ans. 1.8×10^{-10}]

41. Calculate the solubility product of TlBr at 25°C separately from the data given in each of the following:

(*a*) The specific conductivities of water and a satd. solution of TlBr are 2×10^{-7} and 295×10^{-6} reciprocal ohms respectively. The ion conductances are $l_{Ag^+} = 74.7$, $l_{Br^-} = 78.4$.

(*b*) $\Delta G^0_{f(TlBr)} = -39.7$, $\Delta G^0_{f(Tl^+)} = -7.8$ and $\Delta G^0_{f(Br^-)} = -24.6$

(*c*) For the cell, $Tl-TlBr(s) \mid Br^- \parallel Tl^{++} \mid Tl(s)$, the e.m.f. $E^\circ = 0.322$ volt.
[Ans. (*a*) 3.7×10^{-6}, (*b*) 4.5×10^{-6}, (*c*) 3.6×10^{-6}]

42. The solubility product of AgCl is 2.8×10^{-10} at 25°C. Calculate the solubility of the salt in (*i*) pure water and (*ii*) 0.1 *M* $AgNO_3$ solution. (Delhi Univ. '71)
[Ans. 1.67×10^{-5}, 2.8×10^{-9} moles/litre]

43. The solubility product of lead sulphate is 1.3×10^{-8}. Calculate the number of moles of lead sulphate that can be dissolved in 5 litres of 1×10^{-3} *M* sodium sulphate. Show whether lead sulphate will be precipitated if 20 c.c. of 2×10^{-4} *M* lead nitrate is mixed with 80 c.c. of 1×10^{-4} *M* sodium sulphate solution. (Viswabharati '73). [Ans. 6.5×10^{-6} moles]

44. (*a*) The solubility of $BaSO_4$ at 20°C is 2.33×10^{-4} gm/litre. Calculate the solubility product.

(*b*) The solubility product of CaF_2 is 3.2×10^{-11} in water. Calculate its solubility (Delhi Univ. '72) [Ans. (*a*) 1×10^{-12}, (*b*) 2×10^{-4} moles/litre]

II

45. What is Ostwald's dilution Law? How is it experimentally verified? (Rajasthan Univ. '74).

46. Give an account of the theories of acids and bases with special reference to the concept of Bronsted and Lowry and of Lewis. (N. B. Univ. '72)

47. Write brief notes on: (*i*) Buffer solutions, (*ii*) proton theory of acids and bases, (*iii*) Indicator constant, (*iv*) Ionic product of water and (*v*) Hydrolytic constant.

48. What is an indicator? Why does its colour depend upon pH? What indicators should be used in titraling (*i*) HCl with Na_2CO_3 and (*ii*) acetic acid with KOH and why?

49. Discuss the theory of indicators with reference to methyl orange and phenolphthalein. Describe the limitations of their use in acid-base titrations. (Marathwada Univ. '70)

50. What is meant by buffer solutions? Explain their function with a suitable example. How the pH of a buffer solution can be calculated?

51. Explain the terms (*i*) hydrolytic constant and (*ii*) degree of hydrolysis.

Derive an expression for the hydrolytic constant for a salt of a weak acid and a weak base. What is the peculiar characteristic of the degree of hydrolysis in this case?

52. Clearly bring out the significance of solubility product. How are solubility and solubility product related? Show how these can be determined by the conductivity method. Discuss one application of solubility product in analytical chemistry with one example.

53. Account for the following:

(*i*) Sodium bicarbonate is alkaline to litmus but neutral to phenolphthalein.

(*ii*) Addition of excess sodium acetate makes a solution of acetic acid a buffer solution.

(*iii*) The pH of a solution of NH_4OH is decreased on addition of NH_4Cl.

(*iv*) Phenolphthalein is colourless in acidic solution but pink in alkaline solution.

54. Explain why:

(*i*) A solution of sodium chloride is neutral but a solution of sodium acetate is alkaline.

(*ii*) H_2S is a weak acid and yet precipitates copper sulphide from a solution of copper sulphate.

(*iii*) In qualitative analysis, copper is precipitated as sulphide in the second group and zinc in the fourth group.

(*iv*) Calcium oxalate is insoluble in acetic acid but soluble in HCl.

(*v*) Silver chloride is less soluble in sodium chloride solution than in pure water.

(*vi*) Magnesium is not precipitated from a solution of its salt by NH_4OH in presence of NH_4Cl.

55. Justify or correct the following statements with reasons:

(*a*) Both the specific and equivalent conductance of a solution increase with dilution.

(*b*) The ionisation of water is very small, hence ionisation constant and ionic product of water are the same.

(*c*) The degree of hydrolysis of a salt from a weak acid and weak base is highly sensitive to dilution.

(*d*) The solubilities of $CaSO_4$ and $PbCl_2$ shall be the same as both have the same solubility product 2×10^{-4} at 20°C.

(*e*) The pH of 1×10^{-9} *M* HCl solution is 9.0.

(*f*) Methyl orange is a good indicator in the titration of caustic soda by oxalic acid.

CHAPTER 23

INTERFACIAL EQUILIBRIUM : THE CLLOIDAL SYSTEMS

23.1 Phenomena at the Interface: Adsorption

The phenomenon of adsorption has been briefly defined in connection with the heterogeneous catalysis in Sec. 18.4. It has also been noted that there are broadly two types of adsorption, (*i*) *Physical* or *van der Waals adsorption* and (*ii*) *chemisorption* or *Langmuir's adsorption.* The characteristics of adsorption will be briefly dealt with here.

Adsorption is an exothermic process. Therefore, in all cases adsorption decreases with rise in temperature. The two types of adsorption mentioned above can be distinguished from the following:

(*i*) Physical adsorption does not exhibit any specificity and depends only on the nature of adsorbate. The chemical adsorption is quite specific depending upon the nature of both the adsorbate and the adsorbent.

(*ii*) Physical adsorption is more pronounced at temperatures below the boiling pt. of the adsorbate whereas chemisorption occurs usually at high temperatures.

(*iii*) The physical adsorption equilibrium is readily established and is reversible. In chemisorption, the attachment is much stronger, the equilibrium is attained slowly and is mostly irreversible in the sense that desorption does not occur on reduction of pressure.

(*iv*) In physical adsorption, the heat of adsorption is relatively small, about 5 Kcal/mole which is of the same order as that of vaporisation. In chemisorption, the heat evolved is larger, about 20 ~ 100 Kcal/mole, as often found in chemical reactions.

(*v*) In physical adsorption usually multilayers are formed whereas in chemisorption ordinarily a unimolecular layer is formed.

23.2 Gibbs Adsorption Equation

In 1878, J. Willard Gibbs showed from thermodynamic considerations that the concentration of a solute could be higher at the surface of the solution than that in the bulk of the solution. The excess concentration depends on the surface tension of the solution at any given temperature T. He also established a quantitative thermodynamic relation, as

$$\Gamma = -\frac{c_2}{RT}\cdot\frac{d\gamma}{dc_2} \qquad \ldots \text{(XXIII.1)}$$

where Γ = excess conc. of the solution per unit area of the surface
c_2 = Conc. of the solute in the solution
$d\gamma/dc_2$ = rate of change of surface tension with the concentration, c_2

This is known as the *Gibbs Adsorption Equation.*

Usually $d\gamma/dc_2$ is negative and so Γ is positive, *i.e.* there would be excess concentration of the solute at the interface. For some solutions, $d\gamma/dc_2$ is positive, *i.e.* Γ is negative, the conc. of the solute in such cases would be less at the surface than that in the bulk.

The experimental verification of the Gibbs adsorption eqn. was first carried out by McC. Lewis. A stream of drops of mercury or hydrocarbon oil were run slowly down a column of an aqueous solution of a dyestuff or caffein. At the surface of the mercury (or oil) drops, the solute was adsorbed. The initial concentration and the final concentration of the solute in the bulk-phase were measured. The difference gave the total amount of solute adsorbed. The total area of the surface of the mercury (or oil) drops were calculated from a knowledge of the total quantity of the mercury and number of drops run down. Thus the value of Γ_2, the adsorbed amount of solute per sq. cm. was known. The right-hand side of the equation (XXIII.1) was also separately determined by directly measuring surface tension at various concentration c_2. The slope of the curve (γ vs. c_2) gave the value of $\frac{d\gamma}{dc_2}$ and the expression $-\frac{c_2}{RT}.\frac{d\gamma}{dc_2}$ was calculated. The agreement between the two was fairly satisfactory. Later on, Donnan and Barker repeated the experiments with aqueous solutions of nonylic acid and saponin using bubbles of air in place of mercury droplets.

The relation between the amount adsorbed by the adsorbent and the pressure (or concentration) of the adsorbate at a constant temperature is called the *adsorption isotherm*. Two such adsorption isotherm relations are in use.

23.3. Freundlich Adsorption Isotherm

The variation of adsorption of a gas with pressure is often expressed empirically as

$$\frac{x}{m} = kp^{\frac{1}{n}} \qquad \ldots \text{(XXIII.2)}$$

where x gm of gas are adsorbed by m gm of adsorbent at pressure p, so that x/m denotes the amount of gas adsorbed by unit mass of the adsorbent. n and k are constants depending upon the nature of adsorbate and adsorbent. n is always greater than unity, which means that the amount of adsorption does not rise as

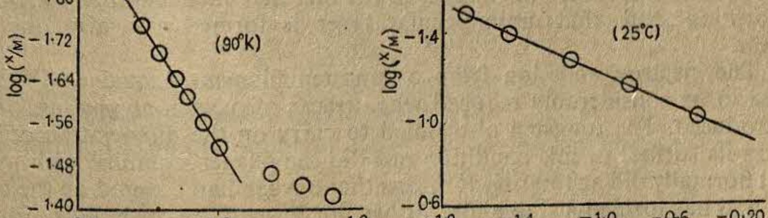


Fig. XXIII.1. Adsorption isotherm. (*a*) N_2 on mica at 90° K
(*b*) Acetic acid on charcoal at 25°C

rapidly as the pressure. Taking logarithms of both sides, equation (XXIII.2) becomes

$$\log \frac{x}{m} = \log k + \frac{1}{n} \log p \qquad \ldots \text{(XXIII.3)}$$

This relation was extensively used by Freundlich in measurements of adsorption and is often called **Freundlich isotherm.** A graphical representation of log x/m against log p would therefore give a straight line. This relation is an approximate one and is suitable for small ranges of pressure (Fig. XXIII.1).

This isotherm is also generally used for adsorption of solutes from solution and has been found satisfactory. The pressure in the expression is replaced by equilibrium concentration (c) of the solute, *i.e.*,

$$\frac{x}{m} = kc^{\frac{1}{n}}, \quad \text{or,} \quad \log (x/m) = \log k + \frac{1}{n} \log c \qquad \ldots \text{(XXIII.4)}$$

k and n are empirical constants depending on the system and the temperature. The relation can be tested quite easily. A known quantity of blood charcoal may be added to equal volumes of dilute solutions of acetic acid at different concentrations and shaken at a constant temperature. The concentration of the acid at equilibrium is then determined by titration. Log (x/m) plotted against log c gives a straight line, from the slope of which $1/n$ can be easily obtained.

23.4. Langmuir's Adsorption Isotherm

In the adsorption of gases on solids, according to Langmuir the solid surface is a pattern of regularly arranged solid atoms, each of which has a residual field of force extending outwards (Fig. XVIII.3). A gas molecule approaching the surface gets linked up by loose sharing of electrons on a surface atom. This is *chemisorption* as the linking is more or less through sharing of electrons. Once the surface is covered up by the gas molecules, no further linking of the gas molecules would occur and the adsorbed gas layer is unimolecular in thickness. Some of the adsorbed molecules however would have a tendency for evaporation or desorption. But soon an equilibrium is set up when the rates of adsorption and of desorption become equal.

Experimental evidence in support of the fact that chemical forces are involved in adsorption and that unimolecular layer is formed was also obtained by Langmuir.

(*i*) The electron emission from a tungsten filament heated at 1900°K was observed to be considerably reduced when traces of oxygen at pressure 10^{-6} atm was introduced. The tungsten also failed to carry on the dissociation of H_2 into atoms on its surface in this condition nor did the oxygen combine with hydrogen which it normally did at 1500°K. It means that oxygen had covered up the tungsten surface and has formed a stable film. It has not formed the oxide WO_3, for in that case WO_3 would distil away even at 1000°K. In fact, on prolonged heating tungsten oxide was formed which evaporated off leaving clean solid surface and electron emission was restored. Such a stable nature of the oxygen-film on the tungsten clearly indicated the chemical nature of adsorption.

(*ii*) On studying the adsorption of N_2, Argon, CO, CH_4, etc. on smooth surfaces of glass, mica and platinum, Langmuir found that in every case about 0.6×10^{15} molecules were adsorbed per sq. cm. The constancy of this value indicated that layers of same thickness were formed in each case. Assuming interatomic distance on the crystal lattice to be 3Å, the number of surface atoms per sq. cm. is also of the order of 10^{15}. It is therefore reasonable to conclude that unimolecular films are formed on the surface.

The unimolecular nature of oil films on water was also directly demonstrated by Langmuir (see later).

Langmuir also deduced a relation between the amounts of adsorption and the pressure. Let μ be the mass of gas striking per sq. cm. of the surface per second of which α fraction gets adsorbed. Suppose θ is the fraction of the surface already covered by adsorbed gas molecules, the bare portion of the surface where fresh adsorption may occur is $(1-\theta)$. Then,

Rate of adsorption $= \alpha(1-\theta)\mu$, and rate of desorption $= \beta\theta$, where α and β are constants for a given system.

At eqm. the two rates are equal, *i.e.*, $\alpha(1-\theta)\mu = \beta\theta$

i.e.,

$$\theta = \frac{\alpha\mu}{\beta+\alpha\mu} \qquad \ldots (A)$$

Now suppose η gm-moles of gas are adsorbed per unit area. Assuming the surface to be uniform η is proportional to the quantity adsorbed per gm of the adsorbent, *i.e.*,

$$\eta = z_1 \frac{x}{m}\ ; \ (z_1 \text{ is a constant})$$

The number of molecules adsorbed per sq. cm. is ηN_0 where N_0 is Avogadro number. Further suppose there are N_s atoms of adsorbent present per unit area of surface where adsorption could take place· The fraction of surface covered by adsorption (θ) is thus $\frac{\eta N_0}{N_s}$ assuming unimolecular thickness of the adsorbed layer. So

$$\theta = \eta \frac{N_0}{N_s} = z_1 \frac{x}{m}.\frac{N_0}{N_s} = z_2 \frac{x}{m} \qquad \ldots (B)$$

remembering that N_s is constant for a given system.

From the kinetic theory it is found that μ, the mass of gas striking per unit area is given by

$$\mu = \sqrt{\frac{M}{2\pi RT}}.P = z_3 P \qquad \ldots (C)$$

where P is the pressure at the constant temp. T.

Substituting (B) and (C) in (A),

$$z_2 \frac{x}{m} = \frac{\alpha z_3 P}{\beta+\alpha z_3 P}$$

or

$$\frac{x}{m} = \frac{k_1 k_2 P}{1+k_1 P} \qquad \ldots (XXIII.5)$$

where constant $k_1 = \frac{az_3}{\beta}$ and $k_2 = \frac{1}{z_2}$, (α, β and k-terms are all constants).

This relation between the pressure and the amount adsorbed at a constant temperature is the *Langmuir adsorption isotherm*. Rewriting,

$$\frac{P}{x/m} = \frac{1}{k_1k_2} + \frac{P}{k_2} \qquad \text{.. (XXIII.6)}$$

That is, if $\frac{P}{x/m}$ be plotted graphically against P, a straight line is predicted. This has actually been experimentally realised in many cases of adsorption.

23.5. Surface Films on Liquids

Minute quantities of oil added to water will spread and form thin films on the surface. Other insoluble substances such as long chain fatty acids like stearic acid, oleic acid, etc. also spread out on the surface of water. The spreading is to be regarded as a case of adsorption of one liquid on another.

When a long chain fatty acid, say stearic acid, $CH_3(CH_2)_{16}COOH$, comes in contact with water,$-COOH$ group is strongly attracted towards water while the hydrocarbon chain is hydrophobic and prevents it from dissolving. The net result is that it spreads out and generally forms, as we shall see, a unimolecular layer on the water surface. The study of such surface films is nowadays made with a Langmuir film balance (Fig. XXIII.2).

A shallow tray is filled to the brim with water. A light mica float just less than the width of the trough is placed on water at a fixed position near one end. At the extremeties of the float two thin Pt-strips are attached to prevent any leakage of an oil film on the surface. The float is rigidly attached through an unspun silk fibre to a delicate torsion wire balance placed vertically above this mica float. It is thus possible to measure any lateral pressure on the float from the torsion balance. Near the other end of the trough placed on water is a movable barrier of thin glass plate placed parallel to the float. The barrier is mounted on a screw moving along a scale, so that the area between the float and the barrier is easily known. From a microsyringe a drop of a benzene solution of stearic acid of known concentration is added to the surface of water. The benzene evaporates off and an oily film spreads on the surface of water between the float and the barrier. The quantity and hence the number of molecules of stearic acid on the surface is known.

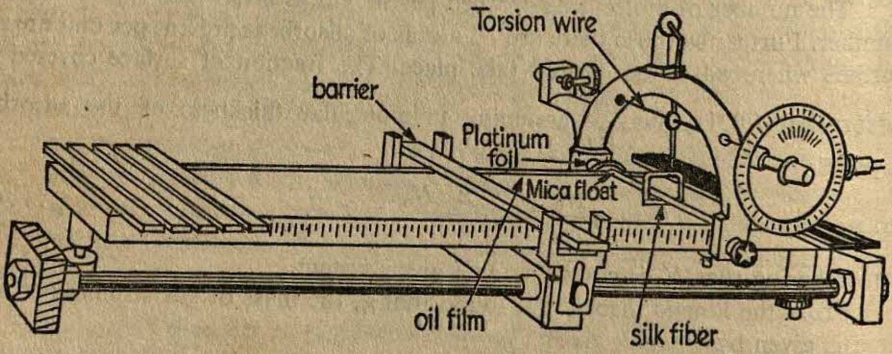


Fig. XXIII.2. Langmuir film balance

So long the area is relatively large, the molecules in the oily film move about freely as is evident from the motion of the lycopodium dust added on the film surface. The barrier is then pushed slowly towards the float, *i.e.*, the area of the oil film is reduced. In such compression of the film, initially no change in the lateral pressure on the float is noticed from the torsion balance. But soon a critical limit of compression of the area is reached. Suddenly at a point the film becomes rigid, the dust particles do not move and fine strain lines begin to appear on the film. At this point, any attempt to reduce the film area even slightly is found to register in the balance a sudden steep-rise in the lateral pressure on the float. Further contraction of the area crumples up the film altogether. If the pressure on the float is plotted against the surface area per molecule, a curve of the type shown in Fig. XXIII.3 is obtained. At some point, the film becomes rigid and the lateral pressure rises steeply, after which the film buckles and folds on further reduction of area. When this critical point is reached, the area per molecule is found to be 20.5Å². It is most significant, the same critical limit of area (about 21Å²) is obtained when other long-chain fatty acids, from palmitic $C_{15}H_{31}COOH$ to cerotic acid $C_{25}H_{51}COOH$ were used. This area is thus independent of the length of the carbon chain.

From these observations, it is justifiably reasoned that initially the surface was not completely covered by the film and the molecules could freely move about on the surface. On compression of the area a point is reached when the molecules are most close-packed, the entire area is just covered by the film molecules forming a monomolecular layer; any attempt to compress it further is opposed by the film. That the same result is obtained with different acids shows further that the molecules in the film must be similarly oriented having their $-COOH$ groups in water and hydrocarbon residues away from water. The physical picture would be somewhat like that shown in Fig. XXIII.4.

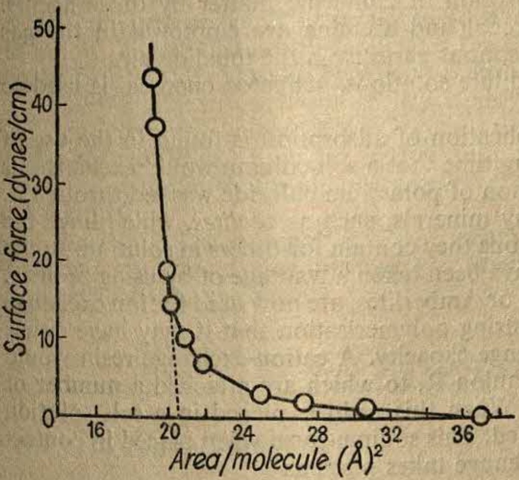


Fig. XXIII.3. Pressure-area isotherm for surface film on liquids

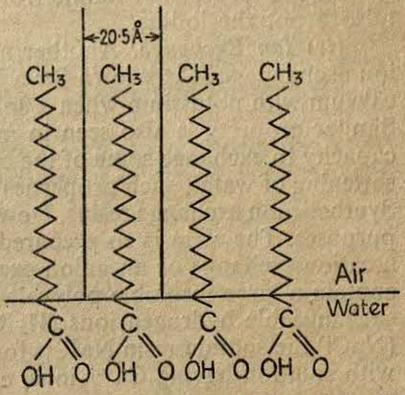


Fig. XXIII.4. A monomolecular oriented surface film on water

Langmuir experiments provide an incredibly simple method of obtaining molecular cross-section. Moreover, these results are found to be quite close to the accurate measurements from X'ray diffraction. The micro-photographs from the infra-red spectroscopy also support the formation of mono-molecular thickness of the film.

The minimum area (21Å²) occupied by a molecule has been found to be independent of the length of the hydrocarbon chain when any of the following polar groups are present at the terminus of the molecule:

$$-COOH, -CONH_2, -COCH_3, -COOR, -OH, \text{etc.}$$

These simple but convincing experiments by Langmuir and, later on, by Adam and others established (*i*) the surface films are unimolecular in thickness and (*ii*) the molecules in the film are oriented. These features of liquid films were, later on, found to be present in gaseous adsorption on solids as well. [See Heterogenous catalysis].

23.6. Application of Adsorption

There are a wide variety of applications for adsorption, both for industrial and domestic purposes. Some of these are listed below:

(*i*) *Heterogeneous Catalysis*: Many chemical industries are based on heterogeneously catalysed reactions and these are effected through adsorption, mostly of gases on solids. From Haber's synthesis of ammonia to the Fischer—Tropsch synthetic fuel, adsorption plays the most vital role in these industries.

(*ii*) *Refining of sugar solutions, vegetable oils, etc.* The activated charcoal is used in decolorising sugar solutions, Fuller's earth is employed in refining the oils, etc., these are due to the adsorption of colouring matter by those agents.

(*iii*) *Gas masks*: Activated charcoal and alumina are employed in the gas masks to adsorb and remove the poisonous gases from the inhaling air.

In the recovery of iodine from dilute solutions, activated charcoal is used to adsorb out the iodine.

(*iv*) *Ion Exchange:* Another application of adsorption is found in the use of ion exchangers. It is known for a long time that a soil column would exchange its calcium with potassium when a solution of potassium chloride was led through it. Similar property is also seen in many minerals, such as *zeolites*, which have the capacity to exchange some of the cations they contain for others in solution. In the softening of water, such properties have been taken advantage of by using zeolites. Synthetic ion exchange resins, Dowex or Amberlites, are now used for ion exchange purposes. The resin is so prepared during polymerisation that it may have either a cation-exchange or an anion exchange-capacity. A cation-exchange resin would contain a large insoluble polyvalent anion R, to which are attached a number of exchangeable hydrogen ions (H_xR). When this resin is placed in a salt solution (NaCl) the sodium resin NaR is formed. This sodium-form when placed in contact with solution having Ca^{++} ions, exchange takes place as

$$2NaR + Ca^{++} \rightarrow CaR_2 + 2Na^+.$$

Thus, the calcium present in solution is removed in the insoluble form by adsorption and exchange. When the resin has become saturated with Ca^{++}, a concentrated solution of NaCl is run through and the process is reversed, reproducing the sodium-resin. The capacity of a resin to adsorb different ions is dependent on the charge carried by the ions and their size in hydrated form.

(*v*) *Stabilisation of Colloids*: The colloidal particles are stablised due to adsorption of ions on its surface. Otherwise, the particles would come together and coagulate.

(*vi*) The *chromatographic methods*: These are used widely nowadays in separating and analysing valuable and minute quantities of components from a mixture and are also based on adsorption. A suitable adsorbent, often very finely powdered aluminium oxide, magnesium oxide or charcoal, etc. is taken in a long column. The solution containing the components is poured down the column. As the solution trickles down, the solute which is more readily adsorbed is retained in the upper layers of the column together with lesser amounts of the other components. Further down in the column, the less easily adsorbed component would be adsorbed. Thus, a partial separation of the components is effected in the adsorbent column. Subsequently, small amounts of pure solvent are allowed to run down the column very slowly. The less easily adsorbed solutes will be first removed by this solvent from the upper strata. As this runs down further, the latter would be adsorbed in a lower strata. As such distinct layers containing different adsorbed solutes will be formed in the column. The entire column may be taken out and different layers may be cut off separately from which the solutes may be extracted or *eluted* by using sufficient solvent. This, in brief, is the principle involved in chromatography. When the solutes are coloured the separate layers are easily seen and detected. But if the solutes are not coloured the different layers are detected with exposure of the column in ultraviolet light. In 1931, Kuhn first successfully employed it in separating the carotenes. The successful separation of rare earth elements by chromatographic method using fractional adsorption on organic resins is another outstanding illustration.

(*vii*) *Adsorption Indicators:* In the titration of KBr solution with $AgNO_3$ solution, eosin solution is added as an indicator. The ppt. of AgBr adsorbs Br^--ions and in presence of adsorbed Br^--ions, eosin is not adsorbed. Just on passing the end-point of titration, the ppt. adsorbs Ag^+ ions as well as eosin and immediately the ppt. is coloured brick-red (due to adsorption of eosin). This change of colour is very distinct and indicates the end-point. Likewise fluorescein is used in the titration of chlorides by $AgNO_3$. These are called adsorption indicators.

(*viii*) *Surface active agents:* Soaps, detergents, sulphonated alkyl naphthalenes, etc. are often responsible for wetting, and emulsification. These are called surface active agents. These are used for dispersion of oil-like immiscible liquids in water. They are also suitable for removal of dirt and grime. They indeed function through adsorption.

Adsorption plays important role in many other fields, such as painting, waterproofing, mordant dyeing, tanning etc. Some antiseptics or germ-killers also function through adsorption.

THE COLLOIDAL SYSTEMS

23.7. The Colloidal State

Substances like glucose, urea, common salt, etc. when added to water dissolve to form homogeneous *solutions* in which the phase distinction between the solute and the solvent is obliterated. In such solutions, the solutes are molecularly dispersed in the solvent medium and their particle diameter are usually of the order of $10^{-8} \sim 10^{-7}$ cm which are invisible even under the microscope. On the other hand, when powdered sand, glass, charcoal, $BaSO_4$ etc. are added to water, they sink to the bottom under gravity. The minimum diameter of the particles required for sedimentation is ordinarily of the order of 10^{-4} cm. They deposit as a distinct visible phase and can be easily separated.

But there are very fine suspensions in which particles have diameters in the range of $10^{-5} \sim 10^{-7}$ cm. The particles in such cases are aggregates of $100 \sim 10000$ molecules. Hence they are not true solutions although they often appear to be homogeneous to the naked eye. The particles are also not big enough to settle down as a sediment. When a substance is present in such a fine state of subdivision dispersed in another medium, it is said to exist in a *colloidal* state. A colloid is therefore not a special kind of substance but it is a state of existence of any substance in which the particle having sizes ranging between 100 ~ 10000Å would remain dispersed in another medium. Broadly speaking a workable definition of a colloid may be given as follows :

A colloidal system is a two-phase heterogeneous system in which one phase is dispersed in a fine state of subdivision (ranging from 1μ *to* $50m\mu$ *approx) in another medium termed the continuous or dispersion medium.* In actual instances, the size limits are not rigid and may vary on either side but most systems conform to the above description.

The distinguishing features of colloids and true solutions are given below:

Property	*Colloids*	*Solutions*
(1) Particle size	100Å ~ 10000Å	1 ~ 10 Å
(2) Sedimentation	Settles on centrifuge	does not settle
(3) Coagulation	on addition of electrolytes	no
(4) Separation	by dialysis or ultrafiltration	no
(5) Brownian motion	Yes	no
(6) Tyndall effect	Yes	no

Most common are the colloidal systems in which a solid is dispersed in a liquid medium, these are called *Sols*, such as As_2S_3 in water. The dispersion media may be gas, liquid or solid with different disperse phases.

Different colloidal Systems

Disperse phase	*Dispersion medium*	*Name*	*Examples*
solid	gas	Aerosol	Smokes
solid	liquid	Sols	S, $Fe(OH)_3$, Ag, in water
solid	solid	—	Ruby glass, some gems
liquid	gas	Aero sol	Clouds, mists
liquid	liquid	Emulsions	Milk, oil in water
liquid	solid	Gels	Jellies, cheese, curd
gas	liquid	Foam	Froth, soap-foam
gas	solid	Solid foam	Pumice stone

23.8. Sols

The dispersions of solids in liquids, *i.e. Sols*, are broadly classified into *lyophobic* and *lyophilic* sols. Lyophobic sols are solvent-hating and the disperse phase has little affinity for the medium; for example, gold sol, sulphur sol, As_2S_3 sol in water. On the other hand, lyophilic sols are solvent-loving, the disperse phase has a natural tendency to be dispresed in the medium and the disperse particles are highly solvated. Gelatine, glue, agar-agar in water are common examples of lyophilic sols. When the medium is water, the sols are often mentioned as *hydrophobic and hydrophilic* sols. The distinguishing properties of lyophilic and lyophobic sols are given here.

Distinguishing characteristics of lyophobic and lyophilic sols.

Lyophobic sols	*Lyophilic sols*
1. These are prepared with difficulty and are relatively unstable.	1. These are easily prepared and quite stable
2. Small additions of electrolytes cause precipitation.	2. Small quantities of electrolytes have no effect
3. These sols are irreversible.	3. Reversible sols
4. The dispersed particles are not usually solvated	4. The dispersed particles are highly solvated
5. The concentration of the disperse phase is often very low	5. High concentration of the disperse phase is easily obtained
6. The surface tension is the same as that of the medium	6. The surface tension is usually lower than that of the water
7. The viscosity is the same as that of the medium	7. Often highly viscous; the viscosity is much higher than that of the medium
8. The disperse particles can be detected under ultramicroscope	8. The individual particles are not easily detected under ultramicroscope
9. The particles carry a definite positive or negative charge	9. The charge of the particles vary with the pH of the medium
10. Exhibit cataphoretic movement.	10. The cataphoretic movements are not easily observed.

23.9. Preparation of Sols

Lyophilic sols are easily obtained by adding the substances to suitable liquids and, if necessary, warming the same. The colloids of glue, starch, gelatine, etc. are produced by heating them with water.

Lyophobic sols are difficult to produce. There are two ways for their preparation: (*a*) *Condensation method* and (*b*) *Dispersion method.*

(*a*) **Condensation Methods.** It is an indirect process for the preparation of a sol. The substance which is to be dispersed is *generated in situ* by some chemical reaction (or sometimes by physical change) under controlled conditions of temperature, concentration, agitation, etc. to form insoluble particles of the substance having sizes within the colloidal range. The chemical reactions may be different in different cases, such as oxidation, reduction, hydrolysis, metathesis, etc. Certain specific examples rather than a description in general terms will clarify the procedures.

Gold Sol. A gold sol is conveniently prepared by *reduction* of chloroauric acid say with formate or hydrazine.

Sulphur Sol. Sulphur sols are easily obtained by *oxidation* of H_2S solution by oxygen or SO_2 or some dilute oxyacid and then purified.

When a solution of sulphur in alcohol is poured into water a sulphur sol is formed. The addition of a solution of a substance to a solvent in which the solute is insoluble is often a convenient process of preparing a sol.

Nickel Sol. When a benzene solution of nickel carbonyl is heated, a fine nickel sol is obtained through the *dissociation* process, $Ni(CO)_4 \rightleftharpoons Ni + 4CO$.

Silver iodide Sol. To a suitably dilute solution of KI is added $AgNO_3$ solution in a quantity appreciably less than the stoichiometric requirement. Silver iodide, produced by *metathesis*, has particle sizes in the colloidal domain and the whole system is stabilised by a small amount of iodide ions present in solution. The unwanted excess of all ions are removed during subsequent purification by dialysis as described later.

Similar metathetical processes are employed in many instances, such as in preparation of $BaSO_4$ sol from $Ba(SCN)_2$ and $(NH_4)_2SO_4$; As_2S_3 from As_2O_3 and H_2S; silicic acid sol from sodium silicate and hydrochloric acid etc.

Ferric oxide Hydrosol. When small quantities of ferric chloride are added intermittently to almost boiling water, ferric hydroxide is formed in colloidal state. Small quantities of ferric ions, and possibly hydrogen ions stabilise the sol. The excess of hydrochloric acid formed is removed during the purification of the sol. Many such oxide hydrosols, such as aluminium oxide, tin oxide, thorium oxide, etc. are prepared by similar *hydrolysis* of their chlorides or nitrates.

(*b*) **Dispersion Methods.** It is a direct method of pulverising the substance to be dispersed in the medium in the required colloidal size.

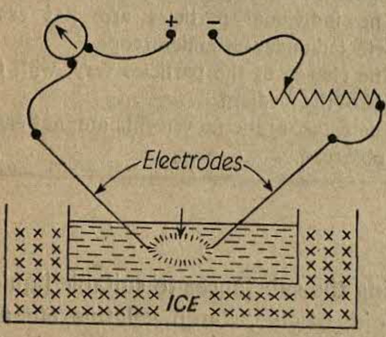


Fig.XXIII.5. Bredig's process

(*i*) *Bredig's Process.* In this process. the pulverisation to the colloidal range is done through electric sparking between two electrodes immersed in the dispersion medium (Fig. XXIII.5). For example, dilute sols of gold, silver, platinum are prepared by bringing close two electrodes of the metal concerned under water so as to permit electric discharge between them. Fine particles of the metal in the colloidal range disperse in the medium.

(*ii*) *Peptization Process.* In this process, a fresh precipitate is taken into a colloidal state on addition of an electrolyte. The precipitate particles adsorb a suitable ion and repel one another and pass into the colloidal state. The electrolyte added is called a peptizing or dispersing agent. For example, a reddish ferric hydroxide *sol* is obtained by adding a small quantity of $FeCl_3$ solution to freshly precipitated $Fe(OH)_3$ and stirring.

$$\begin{array}{ccc} Fe(OH)_3 + Fe^{3+} & \rightarrow & Fe(OH)_3 : Fe^{3+} \\ \text{ppt} & & \text{Sol} \end{array}$$

Peptization is the process by which a stable colloid can be produced from its solid state through addition of suitable agents. Peptization is also sometimes possible from repeated continuous washing of a precipitate with water. Thus when barium sulphate or prussian blue precipitate is washed continuously, a colloidal suspension finally is formed and passes through the filter paper (*iii*) *Colloid Mill.* The substance whose colloid is required is first finely ground and suspended in the medium. This suspension is then passed through a *colloid mill,* which consists of a pair of metal discs almost touching one another and rapidly rotating in opposite directions with high speed. The suspended particles passing in between the discs are pulverised to the colloidal range.

23-10. Purification of the Sols

Colloids prepared especially by chemical methods always contain some excessive quantities of electrolytes and other soluble substances. These have to be removed to obtain a sample of pure colloid. The purification is however carried to a certain limit only as complete purification would lead to instability of the sol.

Substance present as solutes in a true solution or present in a colloidally dispersed state would both pass easily through an ordinary filter paper, As such, it is not possible to separate a colloid from a true solution by filtration. But colloidal particles in the disperse phase are unable to percolate through some membranes such as parchment paper, cellophane, etc. whereas the dispersion medium, ions, solutes of true solutions can easily get through. The process of separation of a substance in true solution (crystalloid) from a colloid by diffusion through special filters is known as *dialysis.*

Dialysis. The sol to be purified is taken in a parchment paper or cellophane bag which is kept suspended in a basin containing sufficient amount of water (or the dispersion medium of the sol if it be not water), as in Fig. XXIII.6. The unwanted ions in the sol move out through the cellophane wall while some amount of solvent from outside may enter the bag. From time to time, the solvent in the basin is replaced and the process allowed to continue for several days. To check the extent of purity, small portions of the sol are pipetted out and its electrical conductance is measured. When the conductance reaches a sufficiently low limit as desired by the experimenter, the process is stopped. Such a process of separation of removal of soluble ions is called *dialysis.*

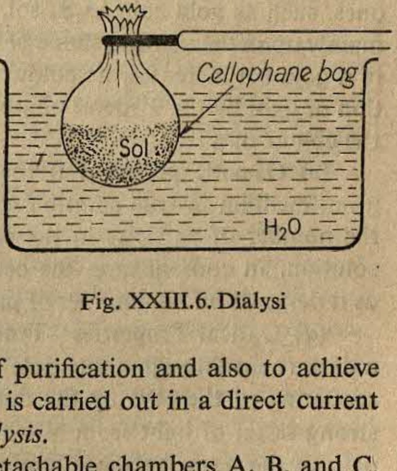


Fig. XXIII.6. Dialysi

Electrodialysis. To accelerate the process of purification and also to achieve a greater degree of purity sometimes the dialysis is carried out in a direct current electric field; the process is then called *electrodialysis.*

A simple electrodialyser consists of three detachable chambers A, B, and C. The middle chamber B which contains the sol is separated on either side from A and C by partitions of cellophane paper D and E (Fig. XXIII.7). The side-chambers A and C are filled with water in which are inserted two Pt-gauze electrodes. A 220-volts direct current field is applied to the system with a carbon-filament bulb in series. On passing electric current, the ionic impurities travel outwards, cations to the negative electrode and anions to the positive. For hastening the process, the water in A and C are drawn out from time to time and replaced afresh. With gradual removal of ions, the resistance increases and the fall in current strength is revealed from the bulb in circuit. The process is stopped when a certain degree of purity is attained.

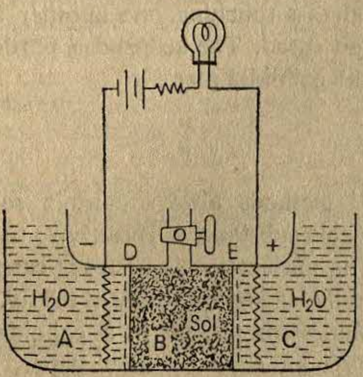


Fig. XGIII. 7. Electrodialyser (diagrammatic)

Ultrafiltration. The pores of an ordinary filter paper are relatively bigger than the sizes of the colloidal particles, which easily pass through. But if an ordinary filter paper be imprergnated with a collodion solution in acetic acid, the pores are considerably reduced in size. Such collodion filters are fixed at the bottom of a cylinder containing the colloid with electrolytes. Pressure is applied on the colloidal suspension in the cylinder, when electrolytes and other solutes and solvent pass through and the colloidal material is left behind. This is *ultrafiltration.* Using graded collodion filters, colloids having uniform particle size can be obtained.

23.11. Properties of Sols

(*a*) **Heterogeneity:** The dispersed particles and the dispersion medium are in two different phases and hence all colloids are heterogeneous systems.

(*b*) **Colour:** Many colloids are brightly cloured, especially the hyophobic ones, such as gold sol, As_2S_3 sol, $Fe(OH)_3$ sol, etc. The colour of a sol depends mainly upon the size and shape of the suspended particles. When the size of particles in a gold sol increases, its colour changes from red to blue. The selective adsorption of light by the disperse phase and the dispersion medium also has an effect on the colour of a sol.

(*c*) **Osmotic pressure:** If the same quantity of a substance be present in a given medium in true solution and in colloidal state, then owing to aggregation the number of particles in the colloid state would be less than that in the true solution. In consequence, the osmotic pressure of the colloid would also be less as it depends on the number of particles only (a colligative property).

(*d*) **Optical Properties—Tyndall Effect:** When a narrow beam of light enters a dark room through a fine hole, its path in the dark room becomes visible due to scattering of the rays by the dust particles. Similar phenomenon occurs when a strong beam of light from a projector is led into a colloid in a dark room. The path of the beam becomes luminescent when viewed from directions at rt. angle to that of the beam. This is due to the scattering of light by the suspended colloid particles. This is known as the *Tyndall effect.* In case a convergent beam made with the help of a lens falls on the colloid, a bright blue cone is observed called the *Tyndall cone.*

The Tyndall effect is pronounced only when the size of the dispersed particles are only slightly smaller than the wavelength of the light used· Moreover, for

Tyndall phenomenon, the refractive indices of the dispersed phase and the dispersion medium should differ appreciably. For this reason, many a lyophilic sol do not exhibit Tyndall effect. True solutions also cannot give Tyndall effect.

Ultramicroscope. Quantitative study of Tyndall effect, and in fact, of other optical and kinetic properties, has been rendered possible with the help of **ultramicroscope,** first employed by Zsigmondy (1903). The visibility of colloidal particles by microscopes is limited by the aperture of the microscope and the wavelength of light used. Even with very good microscopes and with yellow light, the visibility limit is approximately 2×10^{-5} cm. Zsigmondy showed that if the colloidal particles are illuminated by a strong beam from a direction at right angles to the direction of observation through the microscope (*M*) and the colloidal particles be observed against a dark background as in Fig. XXIII.8 the particles become visible as self luminous specks, regardless of dimensions, due to scattering of light. This is the principle in Zsigmondy's ultra-microscope. The specks of light are found to appear and disappear continuously in a chaotic fashion, which indicate that these are in constant motion. These observations confirm the heterogeneity of the colliud system as also the random motion of the dispersed particles.

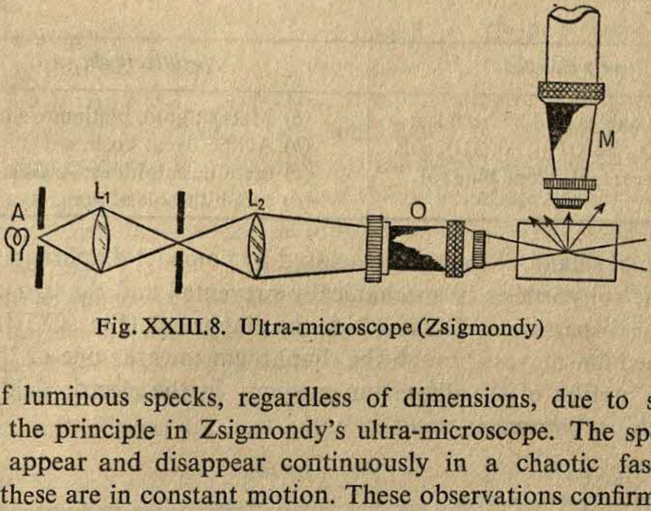


Fig. XXIII.8. Ultra-microscope (Zsigmondy)

(*e*) **Kinetic properties of sols—Brownian motion:** In the latter part of the nineteenth century Brown, a botanist, observed under a microscope that pollen grains suspended in a liquid had a ceaseless chaotic and haphazard movement. Sol particles when examined under a microscope or an ultra-microscope (through Tyndall scattering) are also found to execute random zigzag ceaseless motions. Such movements are called *Brownian motions*. Even when all possible causes which may lead to motions, such as heat, light, mechanical vibrations and other possible disturbances are carefully eliminated, the particles move about ceaselessly for months and months. It is therefore concluded that Borwnian motions are due to molecular impacts from the medium on all sides of these dispersed particles. That the Brownian motion becomes less and less vigorous with the increase in the dimensions of the suspended particles of the sol, as also with the increase in the viscosity of the medium are in conformity with the collision theory proposed.

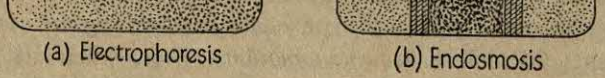
The existence of Brownian motion is an indirect evidence of the existence of molecules and of thermal motion performed by molecules. It also additionally demonstrates that at any instant the numerous impacts suffered by a sol particle on all sides are not evenly matched and this results in a net displacement in a macroscopic time element. There is, however, no preference for directions in these displacements.

(*f*) **Electrical Properties of Sols:** (*i*) **Effect of applied electric field on Lyophobic sols.** If two electrodes are inserted in a lyophobic sol (Fig. XXIII.9a) the disperse phase migrates slowly either to the cathode or to the anode. This indicates that the colloid particles are charged either positively or negatively. In fact, the flocculation of lyophobic sols by addition of electrolytes also suggest the same. The migration of the colloidally dispersed particles in electric field is called *electrophoresis* or sometimes, though not happily, *cataphoresis*.

Some examples of commonly prepared sols with the two types of charges are given here.

Positively charged	*Negatively charged*
(*a*) metallic oxides and hydroxides: TiO_2, V_2O_5, $Fe(OH)_3$, $Al(OH)_3$ sols	(*a*) Metals: gold, platinum, silver sols
(*b*) Basic dyes: methylene blue sol	(*b*) Acidic dyes: eosin sol
	(*c*) metallic sulphides: As_2S_3 sol
	(*d*) lyophilic sols of gum, starch, etc.

On the other hand, if the sol is enclosed by compact diaphragms, so that the motion of the sol particles be mechanically prevented and the two electrodes are inserted in the dispersion medium outside the diaphragm (Fig. XXIII.9b), then the dispersion medium moves through the diaphragm towards one of the electrodes. This relative motion of the dispersion medium in the electric field is known as *electroosmosis* or *endosmosis*.



(a) Electrophoresis (b) Endosmosis

Fig. XXIII. 9

(*ii*) **Effect of addition of electrolytes to lyophobic sols.** It has been stated earlier that while purifying a sol by dialysis the system should not be completely freed from all foreign ions. The presence of small traces of suitable ions is necessary to impart stability to the sol. If the system be divested of all ions, the colloid particles grow bigger and are ultimately thrown out as precipitates.

While small amounts of specific foreign ions are essential, the addition of comparatively larger amounts of a neutral electrolyte proves destructive to the stability of the sol. For example, a small quantity of $NaNO_3$ solution, when added to, say 10 c.c. of a dialysed AgI-sol, will cause the colloidal silver iodide particles to precipitate out as a flocculant gelatinous mass, often called **coagulum,** leaving a clear supernatent liquid. This phenomenon of coagulating the sol particles is known as '*flocculation*'. If insufficient sodium nitrate be added, either no flocculation or partial flocculation will occur. Such coagulation is found with other lyophobic sols also.

Experimental observations on the coagulation of various sols with different electrolytes led to two general conclusions:

(*i*) *Ions carrying the charge opposite to that of the colloid particles are effective in inducing coagulation.*

(*ii*) *The larger the valency of the coagulating ion, the smaller is the quantity of electrolyte (containing that ion) necessary to flocculate a given amount of sol in a given time.*

These generalisations are often mentioned as **Hardy-Schulze rule.**

Continuing with our example of silver iodide sol, it can be coagulated by, say, $NaNO_3$, $Ba(NO_3)_2$, $Al(NO_3)_3$, $Th(NO_3)_4$. Silver iodide sol has negatively charged dispersed particles. So the positive ions Na^+, Ba^{++} etc. are the coagulating ions. This is established from the fact that if NO_3^- ion were responsible for flocculation, then the minimum molar concentrations of the different electrolytes used in equal volumes to coagulate a definite amount of sol completely in just a given time would have been in the ratio 4 : 3 : 2 : 1. But experimentally it is found that the concentrations of ions of higher valency needed is much less than this. Thus if x c.c. of 0.001 M $NaNO_3$ is required, then x c.c. of 0.0001 M $Ba(NO_3)_2$ solution would be quite sufficient for the same coagulation. This proves that oppositely charged ions are responsible for coagulating the dispersed phase and that equicoagulating concentrations of these ions decrease as the valencies increase.

TABLE : EFFECTS OF IONS ON COAGULATION OF LYOPHOBIC SOLS

As_2S_3 (negative) Sol			Fe_2O_3 (positive) Sol		
Electrolyte	*Cation valence*	*Min. conc. millimoles*	*Electrolyte*	*Anion valence*	*Min. conc. millimoles*
NaCl	1	51	KCl	1	103
KCl	1	50	KNO_3	1	131
KNO_3	1	50	KBr	1	138
LiCl	1	58			
			K_2CrO_4	2	0.325
			K_2SO_4	2	0.219
			$K_2C_2O_4$	2	0.238
$CaCl_2$	2	0.65	$K_3Fe(CN)_6$	3	0.096
$BaCl_2$	2	0.69			
$SrCl_2$	2	0.63			
$ZnCl_2$	2	0.68			
$(UO_2)(NO_3)_2$	2	0.64			
$AlCl_3$	3	0.093			
$\frac{1}{2}Al_2(SO_4)_3$	3	0.096			

On the other hand, if the dispersed particles are positively charged as in ferric oxide sol, the anions would be responsible for coagulation and the equicoagulating concentrations of anions (added in equal volumes) would decrease with increase in their valencies. Some data are quoted in the Table from literature in respect of As_2S_3 (negative) sol and Fe_2O_3 (positive) sol.

From an examination of series of such experimental results, Schulze and Hardy framed an empirical rule correlating the equicoagulating concentrations of the different ions with their valences. This relation is

$$C_3 : C_2 : C_1 = 1 : 11.5 : 730$$

where C_1, C_2 and C_3 are the concentrations of mono, bi and tervalent coagulating ions.

(*iii*) **Origin of charge and the mechanism of flocculation:** The conspicuous effect of ions of particular charge type on the coagulation of sol and the latter's behaviour in applied electric field are indicative of the presence of charges on the surface of the colloidal units. The way of acquirement of these charges is mainly by adsorption and, sometimes, by self-dissociation. Structurally a colloidal unit may be viewed as an aggregate of thousands or tens of thousands of molecules forming a sort of microcrystal. These microcrystals have enormous surface area and hence pronounced adsorption characteristics. They adsorb ions, either positive of negative, from the environmental medium in which they are prepared. Often they exhibit a preference for those ions which are common with one of the ions composing the colloidal microcrystal.

Thus the colloidal particles of Fe_2O_3 sol, in its preparation from hydrolysis of $FeCl_3$ by hot water, adsorb Fe^{+++} ions and acquire a positive charge. Fe^{+++}ions are common to both microcrystals and medium. But when Fe_2O_3 sol is prepared from $FeCl_3$ soln with excess of caustic soda solution, the sol particles adsorb OH^- ions and become negatively charged, the hydroxyl ions being common to the medium and the hydrated colloidal particles of Fe_2O_3.

To cite another common instance, the colloidal silver iodide particles have a negative charge due to adsorption of I^- ions when excess potassium iodide is used in its preparation. But if in its preparation excess $AgNO_3$ is used, the resulting sol particles carry a positive charge due to adsorption of Ag^+ions.

The structures of the colloidal units of positively and negatively charged Fe_2O_3 sols, AgI sols, may be expressed as:

(*i*) $[xFe_2O_3, yH_2O]zFe^{+++}$ and $[x'Fe_2O_3, y'H_2O]\, z'OH^-$

(*ii*) $[x_1AgI]y_1Ag^+$ and $[x'_1\, AgI]y'_1I^-$

The preference for common ion adsorption stems from the fact that these ions easily fit in the lattice of the microcrystals.

Sulphide sols, like As_2S_3 sol, are generally stabilised by adsorption of HS^-ions. The charges on metal sol particles are attributed to the adsorption of OH^-ions.

(*iv*) **Stability of Sols:** Owing to adsorption of ions, the dispersed particles in a colloid carry electric charge and hence the particles repel one another. This prevents the particles from coming together and forming bigger particles to precipitate. The charge on the particles is primarily responsible for the stability of the colloid. In the case of lyophilic colloids, the high degree of solvation also prevents aggregation of the particles.

The electric charge on the dispersed particle is firmly fixed on its surface by adsorption. This charge attracts opposite charges from the medium. Ions of opposite charges approach the colloid particles and form a layer in the immediate vicinity of the adsorbed charge. Thus, a double layer of opposite charges is formed at the interface of the dispersed particle and the medium. The opposite charges in the two layers give rise to a potential difference. A qualitative idea can be obtained from Fig. XXIII.10. The double layer is comprised of two parts. The charges in the first section of the double layer (say + ve) remain fixed on the surface at l_1. The solution side of the double layer containing the attracted opposite ions (−ve) can be divided into two parts—(*i*) a fixed part (l_2) of the counter ions at a distance of few angströms from the surface and (*ii*) another diffuse portion of the counter ions with concentration gradually falling off to that of the uniform value existing in the bulk at l_3.

There exists a sharp drop of potential from the solid surface (l_1) to the fixed part (l_2) of the double layer on the solution side. It is then followed by a gradual change in potential across the diffuse part upto the bulk of the solution (Fig. XXIII.10). The total potential drop from the solid surface (l_1) to the bulk of the solution is called the double layer potential ψ, while the difference in potential between the fixed part of the layer (l_2) and the solution bulk (*i.e.*, the potential change across the diffuse portion of the double layer) is termed **zeta potential** or *electrokinetic potential* and conventionally represented by the symbol ζ.

Mechanism of Coagulation: In the negatively charged As_2S_3 sol, each particle carries a number of stabilising HS^- ion on its surface. In the close neighbourhood of this particle, there exists in the solution side one layer of oppositely charged H^+ ions which are more or less fixed and beyond this is the diffuse portion also with H^+-ion predominance. When two such As_2S_3 colloid particles with their accompanying shrouds of diffuse layers approach each other, there is repulsion of similar charges and the particles are prevented from coalescing.

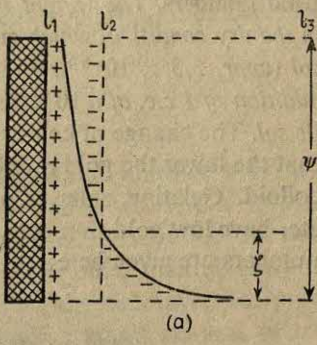


Fig. XXIII.10

If now an indifferent electrolyte, say $BaCl_2$, be added, Ba^{++} ions will be preferentially adsorbed on the fixed part of the solution side of the double layer. The colloidal particle together with the fixed part of the solution side (l_2) will now have a resultant surface density (σ) considerably less than before. The consequence will be the release of a number of H^+ ions from the diffuse part of the double layer. These will migrate to the bulk solution effecting a contraction of the value of the zeta-potential. It follows that, after addition of $BaCl_2$, two As_2S_3 colloid particles can approach nearer because of contraction of the diffuse layer thickness. When the contraction of double layer is quite large, there would be a considerable lowering of ζ-potential, the thermal motions then may overcome the electrical effect and cause coagulation.

For every colloid, there is a critical value of zeta-potential at which coagulation commences, irrespective of the nature of the electrolytes used. For many sols, the zeta-potential value ranges between $0.02 \sim 0.05$ volts.

Lyophilic sols do not coagulate with small concentrations of electrolytes. Considerable quantities of electrolyte solution added to lyophilic systems cause the latter to separate out in clusters called **Coacervates**. This is often called *salting-out*. The salting-out capacity of different ions are different.

It is also found that when two lyophilic systems of opposite charges are brought together, both are salted out.

(*g*) **Protective Action of Lyophilic Sols:** When some lyophilic colloids are added in appreciable amounts to a lyophobic sol, the latter is stabilised and become less sensitive to coagulation even on addition of electrolytes. Lyophilic sols thus play a protective role for many sols.

All lyophilic sols do not afford the same degree of protection to any given lyophobic sol. To measure their protective capacities Zsigmondy set up a standard by which protective capacities are expressed in terms of what is called **Gold numbers.** *The weight in milligrams of the disperse phase of the lyophilic sol in the dry condition, which ought to be added to a* 10 *c.c. portion of a standard Gold sol (appr.* $5.5 \times 10^{-3}\%$ *by wt.) to just prevent its turning from red to blue on the addition of 1 c.c. of a* 10% *solution of NaCl, is called the 'Gold number' of the lyophilic sol.* The change of colour is indicative of the start of flocculation. It is evident that the lower the gold number the greater is the protective action of a lyophilic colloid. Gelatine, salts of protalbic and lysalbic acids obtained from albumen, etc. have low gold numbers and thus high protective capacities. Some of the gold numbers are given here:

TABLE : GOLD NUMBERS OF LYOPHILIC SOLS

Sol	*Gelatine*	*Haemoglobin*	*Albumin*	*Gum arabic*	*Dextrin*	*Potato starch*
Gold number	0.005–0.01	0.03–0.07	0.1–0.2	0.15–0.25	6–20	>25 .

23.12. Gels

Lyophilic sols and some lyophobic sols have the property of setting to a semi-solid jelly-like state at ordinary temperatures, called *Gels*. Lyophilic sols of gelatine, agar, gum arabic, protalbates, mastic, etc. exhibit the gelation property. Of the lyophilic sols, silicic acid sol, ferric phosphate sol, etc. have this property. Many materials of common use are gels, such as curd, fruit-jellies, soaps, boot-polishes, cheese etc. Gels are characterised by high viscosity and considerable swelling if placed in the dispersion medium. For example, if silicic acid gel or gelatine gel be suspended in water, considerable quantity of water is absorbed by the gel and there is a simultaneous swelling of the gel-body. This phenomenon is known as **imbibition**. The most interesting fact in imbibition is that the sum of the net volume of water absorbed and the volume of the gel absorbing it is more than the total volume of the swollen gel. This implies that the structure of a gel is a three-dimensional net-work with large number of void spaces wherein the sorbed molecules of water (or dispersion medium) are accommodated.

Gels, on standing, give out small quantities of liquid (*e.g.* water) which accummulate on the surface. This is known as **syneresis.**

Some gels such as ferric phosphate, ferric oxide, gelatine, etc. when subjected to mechanical shaking lose their semi-solid gel character and acquire the behaviour of sols. They again set to a gel on standing. This phenomenon is known as **thixotropy.** Sometimes, thixotropic gels are obtained by adding electrolytes within certain limits to ordinary sols. Vanadium pentoxide, alumina, bentonite clay also constitute some of the examples of this class. When electrolytes are added, the sols flocculate in the form of gel. If too small or too large quantities of electrolytes are added, gelation does not set in and no thixotropic property is observed.

Tooth-pastes and medicinal ointments placed in tubes are in gel states. Under pressure they flow out more easily due to increase in fluidity. Marshy lands soften on treading and reset on standing. This thixotropic behaviour is due the presence of bentonite clay.

23.13. Emulsions

The colloidal dispersion of the tiny drops of one liquid into another is known as an *emulsion.* Milk, in which tiny fat globules are dispersed in water, is a natural emulsion. Emulsions are often prepared by vigorously shaking together the two liquids. When the emulsions are formed from two pure liquids, their stability is poor and on standing for some time these separate into the two layers of pure liquids. To prepare stable emulsions, it is necessary to add a small amount of an *emulsifying agent.* Soaps of different types, detergents, long chain sulphonic acids, lyophilic colloids such as gelatine, albumin, etc. act as emulsifying agents in different cases. In milk, the protein casein serves as the emulsifying agent. The function of the emulsifying agents is to diminish the interfacial tension.

Emulsions are broadly classified into two types: (*i*) oil in water type in which the disperse phase is the oil in medium water and (*ii*) water in oil type in which water droplets are dispersed in oil. Here the term 'oil' is synonymous with any liquid immiscible with water. The type of emulsion produced depends upon the nature of the emulsifying agent used. Thus, when sodium oleate is used as an emulsifier, an oil-in-water emulsion is formed. But if a soap with a bivalent cation is employed, say calcium oleate, a water-in oil type emulsion is formed.

An emulsion can be diluted with any amount of dispersion medium but the addition of a disperse phase would give rise to a separate layer. If water is added to an oil-in-water type, no change would occur. The addition of oil would produce a separate layer.

Emulsions are most commonly broken up by brisk centrifuging, just as is universally done in separation of cream from milk. Freezing or boiling is also sometimes resorted to. One method of breaking up emulsions is to remove or change the emulsifier by adding external reagents. When soaps are used as emulsifying agents, if the same are hydrolysed by adding acids, the emulsion would easily break.

Fine powders may also act as emulsifying agents, hydrated silica is used for obtaining water-in-oil type emulsion, whereas carbon black is employed to prepare oil-in-water types. An intensive study of emulsions is now encouraged for their varied applications in food, drug and other industries. For example, in the concentration of ores by oil-floatation method, the finely pulverised ore is treated with an oil emulsion such that the required constituent is preferentially adsorbed on the interface for convenient collection.

In everyday use, many emulsions play an important role. Various medicinal emulsions, like cod-liver oil emulsion, are extensively used. Phenyl with water forms antiseptic emulsion. Cleansing property of soap involves emulsifaction of greasy dirt in soap solution.

23.14. Determination of Avogadro Number from Vertical Distribution of Colloidal Particles

The ideal gas laws are obeyed by dilute solutions which suggest that the solute particles undergo chaotic movement similar to those of the gas molecules. The only restriction for the validity of the gas laws in solution is that the solution must be dilute; size of the solute molecules, big or small, makes no difference. If, therefore, we consider solute particles to be so big as can be identified with the kinetic units of a colloidal system, we should expect the kinetic theory considerations to apply to colloidal systems.

The idea of such an applicability of kinetic theory to sols enables one to determine an important physical constant, N_0, Avogadro's number, from a study of Brownian motion in a suspension.

Consider a dilute suspension contained in a tall cylinder. The equilibrium distribution of the sol particles at different heights from the bottom of the container will depend upon the forces acting on the particles. Had the gravity force only been operative, all the sol particles would settle down to the bottom after a time. But the sol particles undergo Brownian motion which have no preference for directions. Take a sol particle at a height h_0 from the bottom and let it undertake certain Brownian displacements in diverse arbitrary directions. The projection of the resultant displacement on the vertical axis will measure the vertical displacement, either upward or downward, of the particle from the reference plane at h_0. It is evident that in the case of downward displacement it aids the gravity force and in the opposite event, the Brownian displacement acts against gravity settling.

The situation is quite analogous to the distribution of pressure and, hence, of molecules of a gas contained in a tall vertical column. The distribution of the gas molecules at different heights is obtained in the following way:

Let the pressure at height, h_0(reference plane) $= p_0$
and the pressure at height, $h_0 + dh_0 = p_0 - dp_0$

The downward thrust of the gas due to the column between h_0 and $h_0 + dh_0$ heights is counterbalanced at equilibrium by the upward thrust (F_0) of the said portion originating from the kinetic motions of the gas molecules.

If σ be the cross-section of the column and ρ_0 the density at height h_0, then

$$\sigma \rho_0 g\, dh_0 = F_0$$

or

$$\sigma \rho_0 g\, dh_0 = -dp_0 . \sigma \qquad \ldots (A)$$

The upward thrust F_0 is equal to $|\, dp_0 \sigma \,|$, the negative sign in (A) is due to the fact that dp_0 denotes increment of pressure.

Again, from kinetic theory.

$$dp_0 = \tfrac{1}{3} mc^2 dn_0 = \tfrac{2}{3} . \tfrac{1}{2}\, mc^2 dn_0 \qquad \ldots (B)$$

where n_0 is the number density of the molecules at height h_0. Substituting $\frac{1}{2}mc^2$ by (3/2) kT per molecule, k being Boltzmann constant, we have

$$dp_0 = kT\, dn_0$$

On introducing this in equation (A),

$$mn_0 g dh_0 = -kT\, dn_0 \qquad (\because mn_0 = \rho_0)$$

or

$$kT \frac{dn_0}{n_0} = -mg dh_0 \qquad \ldots (C)$$

Integrating (C) over a height h_1 to h_2 with the corresponding number densities n_1 and n_2, we have (Fig. XXIII.11).

$$kT\, ln \frac{n_1}{n_2} = mg\,(h_2 - h_1) = mg \triangle h$$

$$\text{Since } k = R/N_0;\ \frac{RT}{N_0}\, ln \frac{n_1}{n_2} = mg \triangle h$$

i.e., Avogadro's number,

$$N_0 = \frac{RT\, ln\, (n_1/n_2)}{mg \triangle h} \qquad \ldots (D)$$

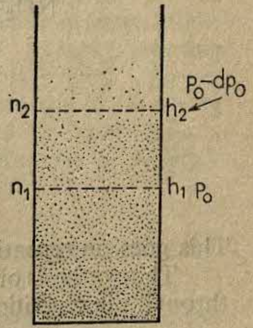


Fig. XXIII.11
Vertical distribution of particles

This relation (D) valid for distribution of molecules in a gas will also hold good for equilibrium distribution of sol particles in suspension. For a homogeneous suspension with spherical sol particles of radius r and with effective density $(d - d_0)$, since the particles are suspended in a medium of density d_0, equation (D) may be written as,

$$N_0 = \frac{RT\, ln\, (n_1/n_2)}{\frac{4}{3}\pi r^3 (d - d_0) g \triangle h} \qquad \ldots (E)$$

The determination of N_0, therefore, demands the experimental measurements of the following quantities:

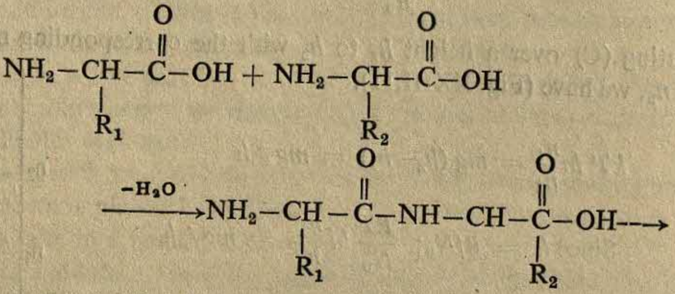
(*a*) n_1 and n_2 or n_1/n_2 at heights h_1 and h_2,
(*b*) $(d-d_0)$, the effective density of the sol particles and
(*c*) the radius r of the sol particles.

In a series of painstaking and laborious investigations Perrin and, later, other investigators determined the quantities involved in equation (E) and evaluated N_0. The value of Avogadro number obtained by them was 6.2×10^{23}.

23.15. Macromolecules

The characteristic behaviour of sols is exhibited when the particle size of the dispersed phase ranges between 100Å and 10000Å. There are many molecules which are large enough to be in the range of colloidal dimensions. Their molecular weights are quite high ranging from, say 5000 to one-million or so. These are really giant molecules, now a-days mentioned as *Macromolecules*. Examples of marcromolecules occurring in nature are those of proteins (gelatine), nucleic acids (*DNA*), polysaccharides (cellulose), polyisoprenes (natural rubber), etc. On the other hand, through polymerisation reactions, molecules of low mol. wt. join up through primary valences into large giant ones by repetitive manner. Thus, ethylene (M = 28) polymerises to give polyethylene of mol. wt. more than 30000. In natural macromolecules also, as in proteins, a large number of similar structural units are joined together by the same kind of linkage. To illustrate, some basic reactions may be cited.

The formation of protein from amino acids is primarily based on a reaction as,



$$\mathrm{NH_2{-}\underset{R_1}{\underset{|}{CH}}{-}\overset{O}{\overset{\|}{C}}{-}OH + NH_2{-}\underset{R_2}{\underset{|}{CH}}{-}\overset{O}{\overset{\|}{C}}{-}OH}$$

$$\xrightarrow{-H_2O} \mathrm{NH_2{-}\underset{R_1}{\underset{|}{CH}}{-}\overset{O}{\overset{\|}{C}}{-}NH{-}\underset{R_2}{\underset{|}{CH}}{-}\overset{O}{\overset{\|}{C}}{-}OH} \longrightarrow$$

This goes on repeating until a giant-size molecule is formed.

The synthesis of nylon from hexamethylene diamine and adipic acid is achieved through the repetition of

$$\mathrm{NH_2(CH_2)_6NH_2 + HOOC(CH_2)_4COOH \xrightarrow{-H_2O} NH_2(CH_2)_6{-}NH{-}CO{-}(CH_2)_4COOH} \longrightarrow \ldots$$

The shape of the macromolecules also varies, some of them are nearly spheroidal, some of them are rod-like, again many of these have coiled chains repeatedly folded. When there are cross-linkings between the units or chains, the macromolecules become rigid which makes them infusible and insoluble materials, such as bakelite, vulcanised rubber etc. The physical character of macromolecules primarily depends on their shape and size. Their true solutions exhibit colloidal characteristics.

23.16. Association Colloids

There are instances where in a solution, with increase in concentration, the solute molecules or their ions come together to aggregate spontaneously to form stable bigger particles of colloidal dimensions. These are called *association colloids* and these usually incorporate into the aggregate appreciable quantity of solvent molecules. The association colloids cannot be regarded as macromolecules as the latter are individual molecules of giant size in solution. They also differ from lyophobic colloids which are thermodynamically unstable. The term '*micelles*' is almost universally employed for the clusters or aggregates formed in solution by association colloids. Although there are some examples of micelle formation from neutral or nonionic molecules, such as polyethylene oxide, but mostly micellizations occur from the large ions of molecules in solution. Usually such molecules have a lyophobic group and a lyophilic group. A typical example of association colloid is that of sodium oleate, $[C_{17}H_{33}]COO^{-}Na^{+}$. The long hydrocarbon part $C_{17}H_{33}$ is the lyophobic portion which tries to recede away from the solvent water. But the 'head' COONa is the ionisable lyophilic group which tends to go into water resulting into ions. When the concentration is quite low say less than 3×10^{-3} *M*, we have a simple solution of sodium oleate. But as the concentration is increased, th lyophobic hydrocarbon parts receding away from the solvent approach each other and form a cluster as in Fig. XXIII.12. The micelle formed is therefore one of anions. The micelle may contain a hundred or more oleate ions clumped together. It is more or less spherical, the hydrocarbon ends are in the interior and—COO⁻ groups projecting outward, in contact with the solvent. It is thus a colloid particle with charges on the surface to which oppositely charged Na⁺ ions would be attracted forming double layers. The name 'colloidal electrolyte' is also often used for such suspensions. Similar micellization with anionic groups are found in other soaps, sulphonates, dyes etc.

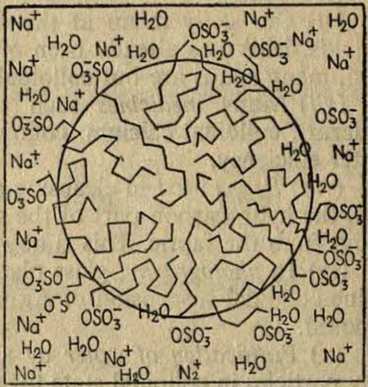


Fig. XXIII.12. Micelle formation long-chain sulphonate (diagrammatic)

23.17. Application of Colloids

Innumerable colloids occur in nature and many colloidal systems are exploited for domestic, laboratory and industrial purposes. Only a few of these are mentioned here.

(*i*) *Clouds and mists* are natural colloids. When air saturated with water vapour reaches a cold region, colloidal particles of water are formed and remain suspended in air.

(*ii*) The atmosphere has a fine suspension of dust particles in it. This is an *aerosol*. These suspended particles scatter the light, for which the sky looks blue. Otherwise if there were no dust particles, the sky would be all dark.

(*iii*) *Soils* are also colloidal in nature. Most of the types of clay present in soil are colloids. The *humus* found in soil is indeed a protective colloid.

(*iv*) The *deltas* formed at the river mouth are results of colloidal activity. The clay and silicates present as colloids are carried over to the river-mouth by the river current. At the mouth, these meet the dissolved electrolytes (NaCl, $MgCl_2$, etc.) of the sea water. The colloidally suspended materials are deposited by the ions of the sea-water and deltas are formed.

(*v*) Blood and many other body-fluids exist in colloidal state. Milk is also a colloid, rather emulsion, having fine fat particles suspended in water protected by casein. Bleeding is stopped by adding alum. This is a case of coagulation of blood by Al^{+++} ions.

(*vi*) Our daily menu at the dinner-table often contains a large number of colloids. Milk has already been mentioned. Butter, cheese, Ice cream, fruit-jellies, curd, many soups are but colloidal in nature.

(*vii*) Many *medicines* such as colloidal sulphur, colloidal antimony (for Kalazar), colloidal calcium, colloidal silver (protargol) are used in this form for better efficiency.

(*viii*) *Soaps* used in cleansing are association colloids. In removing the greasy dirt, the hydrocarbon part of the soap molecules enters into the grease and drags it out from the fabric. This is how dirt is removed.

(*ix*) In *photography*, glass plates or films are coated with gelatine containing a fine colloidal suspension of AgBr. The colloidal AgBr is effected by light when exposed.

(*x*) *Purification of water* by alum: River or canal water contains suspended clay particles in colloidal state together with bacteria etc. On treatment with alum, the suspended particles coagulate. The presence of $Al(OH)_3$ formed by hydrolysis helps in settling the coagulum.

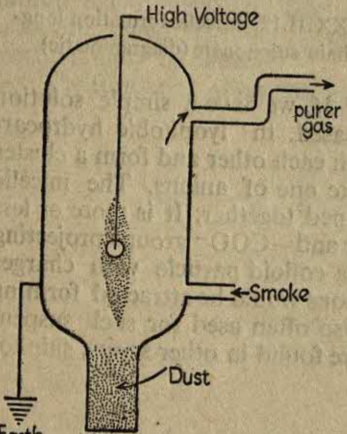


Fig. 23-13. Cottrell precipitation

(*xi*) The *smoke* coming out from the factory chimneys are mostly colloidal suspension of coke in air. In order to avoid pollution, the carbon particles are deposited by Cottrell method. In a vertical column a wire with a knob is charged to a high potential. The charged colloidal carbon particles are attracted to the knob. These lose their charge and fall down as a precipitate. The purer gas escapes to the atmosphere.

(*xii*) In the modern *sewage disposal* scheme, the suspended particles mixed with excess water are led through a strong field. Due to electrophoresis, the particles move to the electrodes and coagulate there. These are used as manures.

(*xiii*) Many *industries*, such as dyeing, tanning, black polish, rubber industry, etc. are primarily based on colloidal suspensions.

EXERCISES

1. Distinguish between adsorption and absorption. What do you understand by physical adsorption and chemisorption?

2. Discuss Langmuir's theory of adsorption and derive an expression for Langmuir's monolayer adsorption isotherm.

3. Write brief notes on:

(*i*) Gibbs adsorption isotherm

(*ii*) Chemisorption

4. Give an account of the Freundlich adsorption isotherm. Describe an experiment to verify this isotherm.

5. Write informative notes on:

(*i*) Adsorption from solution

(*ii*) Surface films of insoluble substances with polar groups

(*iii*) Adsorption on solid-gas interface

(*iv*) Activated adsorption

6. The following data were recorded in an experiment on the adsorption of acetic acid from aqueous solution by charcoal:

Conc. of solution (c)	3.6×10^{-3}	8.4×10^{-3}	20.0×10^{-3}	35.0×10^{-3} gm/c.c.
adsorption (x/m)	0.018	0.022	0.028	0.032

Show that the results conform to Freundlich isotherm.

7. In an adsorption of a gas on charcoal the following results were obtained:

P (dynes/cm^2)	3.0	4.0	6.0	9.5	17.0
mass of gas adsorbed (mg/cm^2) $\times 10^3$	14.2	17.6	22.0	28.0	33.0

Examine graphically to what extent Langmuir's equation is applicable.

8. At 0°C, nitrogen was adsorbed on charcoal at different pressures p. The amount of gas adsorbed is expressed in c.c. at N.T.P.

p (*mm*)	3.90	13.0	23.0	34.0	56.5
v (c.c./gm)	0.99	3.00	5.05	7.00	10.4

Plot the data according to Langmuir isotherm and find out the value of constants of eqn. XXIII.5.

9. Explain, with illustration:

(*i*) the purification of water by ion-exchange method

(*ii*) the separation of products by chromatographic method

(*iii*) the estimation of silver by adsorption indicators.

10. Explain the term 'colloidal solution'. Describe different methods used for preparing colloidal solutions. Discuss their electrical and optical properties, (*Delhi Univ.* '71; *Allahabad* '71).

11. Describe the different methods of preparing colloidal solutions. Give an example of each. Explain how these solutions are (*i*) stabilised and (*ii*) coagulated. (*Viswabharati* '73).

12. How would you prepare colloidal solutions of (*i*) gold (*ii*) ferric hydroxide and (*iii*) arsenious sulphide? Describe the electrical and optical properties of colloidal solutions.

13. Describe the properties of colloidal systems and outline the theories of their stability. (*London* '74).

14. Define and distinguish between lyophilic and lyophobic colloids. Explain Schulze—Hardy Law. What is zeta-potential?

15. What factors contribute to the stability of a coloidal solution? Explain why a colloidal solution is not precipitated on the addition of an electrolyte in presence of gelatine.

16. Write notes on:

(*i*) Gold number, (*ii*) Electrophoresis, (*iii*) peptisation, (*iv*) coagulation.

17. How is a colloid purified? How would you show that colloidal particles are charged? How would you find out the nature of their charge?

18. What is the origin and significance of charge on a colloid particle?

19. Explain and illustrate: (*a*) Dialysis, (*b*) Hardy-Schulze Law, (*c*) peptisation, (*d*) Gold number, (*e*) emulsions.

20. Explain: (*a*) detergent action of some colloids, (*b*) use of alum in purification of town-water supply, (*c*) formation of deltas at the mouth of many rivers, (*d*) precipitation of carbon particles from smoke by Cottrell method.

21. What type of colloids are the following: (1) guava jelly, (2) milk, (3) gold sol, (4) rubber latex, (5) coating on the photographic plate, (6) butter.

CHAPTER 24

THE STRUCTURE OF THE ATOM

In the last decade of the nineteenth century, J. J. Thomson (1897) discovered that the negatively charged particles (called electrons) existed in the atoms. Simultaneously Becquerel (1896) discovered the radioactive phenomenon in which subatomic particles were emitted spontaneously from heavier atoms. Dalton's concept (1803) that of the indivisibility of atoms and that atoms were the ultimate fundamental particles of matter had to be discarded. A brief outline of these two phenomena may first be given.

24.1. The Cathode Rays: Electrons

For a long time it was known that if gases maintained at very low pressures were subjected to high potential, they became conducting and there were luminous effects. At a pressure of the order of 0.01 mm, the glass tube containing the gas remains dark (*Crooke's dark space*) but a streak of rays, called the **cathode rays,** emanate from the cathode. This is confirmed from the fact that a fluorescence is produced on the wall directly opposite the cathode where the rays impinge.

A very careful study of the cathode rays has revealed its many characteristic properties:

(*i*) The cathode rays excite fluorescence on the glass walls where they impinge.

(*ii*) The rays travel in straight lines, confirmed by the shadows of objects placed in their path.

(*iii*) The rays have penetrating power and can pass through thin metal foils.

(*iv*) They also possess considerable momentum: small paddle wheels placed in their path rotate from impact with the rays.

(*v*) The cathode rays are deflected from their path by the application of magnetic or electrostatic field. From the direction of deflection, the charge accompanying the rays is a negative one.

(*vi*) When the rays impinge on a metal target, called *anti-cathode,* placed on the path, a different type of radiation, *the X-rays*, is produced. These new radiations are not deflected in an electric or magnetic field. X-rays are really electromagnetic radiations of very short wave lengths.

The cathode rays were found to consist of streams of *negatively charged particles*, called **electrons** and this was first established by J. J. Thomson (1897). He also succeeded in determining the ratio of its charge to its mass (*e*/*m*).

Not only in the cathode rays, electrons are produced from other sources, *e.g.* (*i*) Some metal filaments when strongly heated emit electrons, (*ii*) Various matters on exposure to X-rays emit electrons, (*iii*) Alkali metals when exposed to ultraviolet radiations give out electrons, (*iv*) β-rays emitted by radioactive substances have also been found to consist of electrons (see later). The electrons produced from different sources were found to be identical.

24.2. Determination of e/m of the Cathode rays

The experimental arrangement devised by Thomson is shown in Fig. (XXIV.1). A narrow beam of cathode rays emitted from a circular disc cathode C is allowed to pass through a narrow slit of the cylindrical anode A, along the axis of the cathode-ray tube. The pencil of cathode rays ultimately strikes a zinc-sulphide screen S producing a fluorescent spot at P. Two parallel metal plates E, E′ are placed inside the tube such that the beam passes in between them. A difference of potential, say V, is applied to the plates E, E′, when the ray is deflected and the fluorescent spot shifts from P to P′. Subsequently, a magnetic field H produced by an electromagnet (shown by dotted circle) is also applied. The magnetic field will also deflect the beam. Applying the magnetic field perpendicular to the electric field and acting in a direction such that the deflection of the beam is opposite, the fields are so adjusted as to keep the beam in its original path, *i.e.*, the fluorescent spot P does not alter. Suppose the mass, velocity and the charge carried by a particle are m, v and e, then the magnetic force acting on the particle is Hev and this is equal to the centrifugal force mv^2/r.

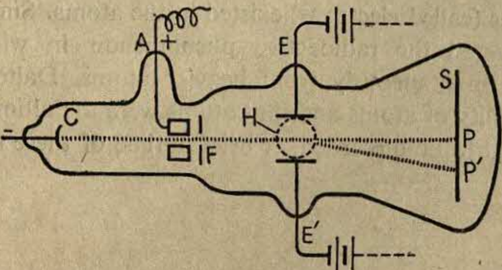


Fig. XXIV.1. Determination of *e/m* (Thomson)

Hence, $$Hev = \frac{mv^2}{r} \qquad \ldots (i)$$

Again, if X be the electric field, the electric force is Xe, so that, under the conditions noted above,

$$Hev = Xe, \qquad i.e., \quad v = X/H \qquad \ldots (ii)$$

Substituting (*ii*) in (*i*), we have,

$$e/m = X/H^2r$$

where r is the radius of curvature of the path of the cathode ray beam under the magnetic field H and can be measured.

The magnitude of *e/m* obtained by Thomson was 1.76×10^8 coulombs per gm.

Several other methods were applied and always the same value was found. Whatever the gas through which the cathode rays pass and whatever the material of the cathode from which they radiate, the ratio of the charge to mass is the same for all cathode rays. Measurements of *e/m* with electrons from other sources, such as emitted from hot filaments etc., gave practically the same value. This confirmed that the *electrons formed a universal constituent of all forms of matter.*

24.3. The Charge carried by an electron

The charge carried by an electron was determined quite early by Townsend and by Thomson using condensation of water-drops on the electrons in a cloud chamber. But an accurate estimation of the electronic charge was first successfully made by Millikan (1909–1916).

(*a*) *Millikan's Experiment.* A diagrammatic sketch of Millikan's apparatus is given in Fig. (XXIV.2). It consisted of a cylindrical vessel *B*, placed in a constant-temperature bath. Inside *B* there were two parallel brass plates *X* and *Y*, *X* being connected to a known steady high potential (say 5000—10000 volts) and *Y* being earthed. There was a pin-hole at the centre of the charged upper plate *X*. The pressure inside was controlled by a pump and a manometer. '*A*' was an atomiser through which very fine droplets of an oil could be injected into the vessel. Two windows *W*, *W* were fitted to the vessel in the opposite walls, in the same line as the parallel plates. Through one window, a momentary beam of X-rays was introduced to ionise the gas in between the plates; a telescope-eyepiece provided with a scale was placed at the other window. The space between the plates was kept illuminated by a light beam from which the thermal rays were cut off by filters.

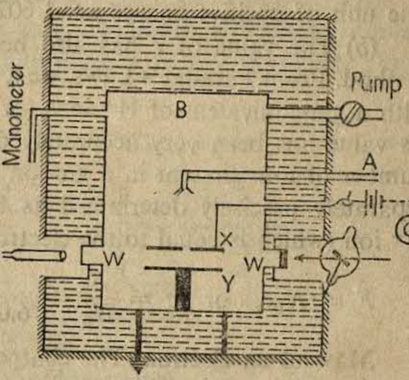


Fig. XXIV.2. Millikan's apparatus for detn. of charge of electron

A droplet of oil, usually positively charged due to friction, sometimes during its sojourn, entered through the pin-hole of the plate *X* and came into view of the eyepiece. Its exact position at any moment could be easily ascertained with the help of the scale in the eyepiece. The droplet, after entering moved downwards towards *Y*, but the field was then applied by charging the upper-plate *X* and the drop would begin to rise towards *X*. When the droplet almost reaches *X*, the field was switched off and the droplet would move downwards under gravity until it would almost reach *Y*, when the field was again applied causing the droplet to move up. In this way, a droplet was moved up and down many times, sometimes several hundred times.

It was found that the droplet while falling under gravity, took always the same time, namely 13.595 seconds to cover a distance of 0.5222 cm. The time was recorded with the help of a high-precision chronograph. But while moving upwards, the droplet needed different time on different journeys under the same field (5051 volts). That is, its velocity upwards varied from time to time. Obviously, the charge on the droplet must have altered.

The minimum variation in the charge of the oil-drop would occur when one electron only would be captured by the drop. From innumerable observations of the upward velocity, the least variation in the charge of the oil-drop was found to be 4.775×10^{-10} esu. Hence, this was rightly considered as the charge associated with an electron. This value did not depend upon the number of trips or the nature of the gas ionised or the oil-drop. The more accurate subsequent investigations showed that the charge carried by an electron is

$$e = 4.802 \times 10^{-10} \text{ esu} = 1.602 \times 10^{-19} \text{ coulombs}$$

This quantity is used as the unit of charge. Thus, the Cl^--ion carries a unit negative charge means that it has a negative charge of 1.602×10^{-19} coulombs; the SO_4^{--} has a negative charge of 3.204×10^{-19} coulombs. The same unit is also applied in the expressing the charges of positive ions. Thus, a Na^+ ion has one unit of positive charge *i.e.* 1.602×10^{-19} coulombs of positive electricity.

(*b*) The value of e has also been very precisely determined by a separate method. From Faraday's Laws, we know that the quantity of electricity associated with a gm-equivalent of H^+ ions (or any other monovalent ion) is one Faraday. Its value has been very accurately determined to be 96496 coulombs. Again, the number of ions present in a gm-ion of hydrogen, *i.e.* Avogadro's number (N_0) is separately precisely determined as 6.0232×10^{23}. If e be charge carried by a H^+ ion (which is equal to the electronic charge), Then

$$F = N_0 e, \quad \text{or} \quad e = \frac{F}{N_0} = \frac{96496}{6.0232 \times 10^{23}} = 1.602 \times 10^{-19} \text{ coulombs}$$

Mass of an electron: The charge of the electron

$$e = 1.602 \times 10^{-19} \text{ coulomb}$$

and it was seen earlier, that

$$e/m = 1.76 \times 10^8 \text{ coulombs/gm.}$$

Hence, the mass of an electron,

$$m = \frac{e}{e/m} = \frac{1.602 \times 10^{-19}}{1.76 \times 10^8} = 9.1 \times 10^{-28} \text{ gm}$$

This is the *rest mass* of the electron. Its mass m' when it moves with a velocity v, is given by the relation,

$$m' = \frac{m}{\sqrt{1-(v/c)^2}}$$

where c is the velocity of light.

Size of the electron: The energy of the electron is e^2/r where r is the radius of the electron. Considering the entire mass as electromagnetic, $E = mc^2$.

$$\therefore \quad mc^2 = e^2/r,$$

$$\text{or} \quad r = \frac{e^2}{mc^2} = \frac{(4.8 \times 10^{-10})^2}{(9.1 \times 10^{-28})(3 \times 10^{10})^2} = 2.8 \times 10^{-13} \text{ cm}$$

The electron is indeed very small in mass and size.

$$\text{The mass of a hydrogen atom} = \frac{\text{a gm atom of hydrogen}}{\text{Avogadro number}}$$

$$\text{or} \quad m_H = \frac{1.0079}{6.0232 \times 10^{23}} = 1.6734 \times 10^{-24} \text{ gm}$$

$$\therefore \quad \frac{m_H}{m} = \frac{1.6734 \times 10^{-24}}{9.1 \times 10^{-28}} \approx 1837$$

Hence, mass of an electron (m) is 1/1837 part of the mass of a hydrogen atom.

24.4. The Positive Rays: Protons

The atom as a whole is electrically neutral. In the cathode-ray discharge tube, when electrons are stripped off the residual portions of the atom must carry a positive charge. This was experimentally demonstrated by Goldstein, Thomson and others. Using a perforated cathode in a discharge tube, as in Fig. (XXIV.3), it was shown that a beam travels through the cathode-holes in a direction opposite to that of the cathode-rays and produces fluorescence on a ZnS screen placed behind.

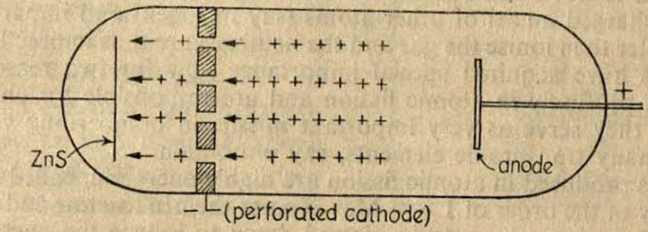


Fig. XXIV.3. The positive rays (diagramatic)

These rays consist of positively charged particles and are called **positive rays** or canal rays. The *e/m*-values of the positive-ray particles are quite low, indicating that the particles are heavier. The *e/m* ratio also varies with the different gases used. It was obvious that they are produced when electrons are stripped off from the neutral atoms under strong electric field. Since the mass of the electron is very small, the mass of the positive ray particle would be almost the same as that of the atom and hence would be different for different gases. To mention their characteristics:

(*i*) They consist of positively charged particles having masses virtually equal to those of the atoms from which they originate.

(*ii*) They move linearly and can penetrate thin metal foils. They also ionise gases.

(*iii*) They are deflected by electric and magnetic fields but in directions opposite to those of the cathode rays. This indicates that they carry positive charges.

(*iv*) Their *e/m* values are low. The particles are much heavier than the electrons.

The lightest positively-charged particle was detected when hydrogen gas was used in the discharge tube. It has the maximum *e/m*-value of all the positive ray particles. It has nearly the same mass as the hydrogen atom. This particle is indeed *a hydrogen atom that has lost an electron and is thus left with a unit positive charge.* This particle has been named a Proton by Rutherford (1922). The proton which is the positively charged H^+ ion is often written as '*p*'. Subsequently it has been found that the proton (like an electron) is a fundamental particle in the building up of atoms. All atoms must contain protons. The proton has a mass of 1.007276 amu and it carries a unit-positive charge.

24.5. The Neutrons

In 1920, Rutherford predicted that particles having masses equal to that of a proton but carrying no charge should exist in an atom. It was as late as in 1932, Chadwick discovered these neutral particles when beryllium was bombarded with α-particles.

$$^{9}\mathrm{Be} + {}^{4}\alpha = {}^{12}\mathrm{C} + {}^{1}n$$

Neutrons, expressed as ^{1}n, can now be produced in various other ways. The neutron is also found to be a fundamental particle in the constitution of an atom. Excepting the ordinary hydrogen atom, all other atoms must contain one or more neutrons.

Since the neutron is electrically neutral it cannot ionise other atoms and hence its path is not detectable in the cloud chamber. Neutrons are allowed to collide with charged nuclei of other atoms (say nitrogen) and impart energy into them. The latter then ionise the gas and the neutrons are thus indirectly detected.

Neutrons have acquired special importance now for two reasons: (*i*) they are produced profusely in atomic fission and are responsible for chain reactions there in, (*ii*) they serve as very important missile in bombarding various nuclei to produce many transuranic elements, say plutonium.

Neutrons produced in atomic fission are highly energised, called fast neutrons having energy of the order of 1 ~ 6 Mev. To use them in reactors and other nuclear processes, the neutrons have to be slowed down to reduce the energy. The low-energy neutrons are called *thermal neutrons* having energy less than 1 ev. The thermalisation is carried out by passing the fast neutrons through graphite, paraffin, heavy water etc. called moderators.

An atom is built up of three types of fundamental particles; protons, neutrons and electrons. Their mass and charge are:

Particles	*proton*	*neutron*	*electron*
mass :	1.007276	1.008665	0.000548 (amu)
charge :	$+1e$	0	$-1e$

[$^{16}\mathrm{O} = 16.0000$; $e = 1.602 \times 10^{-19}$ coulombs]

It would be useful now to be acquainted with the elementary definition of radioactivity and radioactive radiations which provide additional evidence for the existence of subatomic particles.

24.6. Radioactivity & Radioactive Radiations

In 1896, the French scientist Becquerel while investigating the nature of X-rays found that a photographic plate wrapped in thick black paper was affected by a sample of potassium-uranyl-sulphate placed over it. In fact, any uranium compound would affect the plate though covered by paper and kept away from light. Obviously, some radiations emanated from uranium could penetrate the cover and attack the photographic plate. Bacquerel christened this amazing behaviour as **radioactivity**. These radiations were highly penetracting (like X-ray), they affected photographic plates, they ionise gases and produce fluorescence on certain substances. They are not influenced by heat, light or chemical composition. Because of their ionising power they could be easily quantitatively measured with the help of charged gold-leaf electroscopes. Very soon, Marie Curie and Pierre Curie (1898) isolated two other elements—radium & polonium—which were more radioactive than uranium. Since then many other radioactive elements have been discovered. The radioactivity is essentially an *atomic* property. The phenomenon is associated with atoms which are heavier than lead or bismuth.

Radioactive Radiations: In the radiations emanating from radioactive substances, three different kinds of rays have been found, *alpha-*, *beta-*, and *gamma-rays*. Of these, α and β-rays are deflected in magnetic and electrostatic field indicating that they consist of charged particles. The γ-rays are wave motions of very small wavelengths (like X-rays) and are not affected by magnetic or electric fields. This difference can be very easily shown by a simple experiment, similar to that originally done by Becquerel and others. In a deep groove in a block of lead, a minute quantity of a radioactive sample is taken (Fig. XXIV.4). The lead block is kept in an evacuated chamber and a photographic plate (P) is fixed on the wall of the chamber opposite to the open end of the groove. Now a strong magnetic field at rt. angles to the plane of the paper and in a direction away from the reader is applied, when α-rays, are deflected to the left, β-rays to the right and γ-rays remain undeviated, producing dark images in the plate.

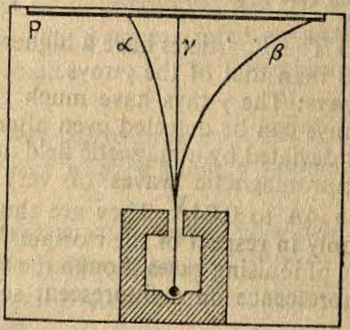


Fig. XXIV. 4.

α-rays: (*i*) The α-rays are made up of positively charged particles (α-particles).

(*ii*) Each α-particle has a mass equal to four times the mass of a hydrogen atom and carries two units of positive charge. [$e=9.3 \times 10^{-10}$ esu, $e/m=4820$ emu/gm]. The α-particle is indeed the doubly charged He-nucleus.

(*iii*) The velocity of the α-particles is about one-tenth the speed of light.

(*iv*) Their penetrating power is relatively less, it is completely absorbed by 1 mm thick lead foil. (β-rays can pass through 3 mm thickness of lead and γ-rays are stopped by 15 cm of lead).

(*v*) They have very high ionising power.

(*vi*) They strongly affect photographic plates and produce scintillations on a ZnS screen.

That the α-particle is a doubly-charged helium nucleus was also experimentally demonstrated by Rutherford.

An apparatus as in Fig. XXIV. 5 was used for the purpose. In a thin-walled tube A a quantity of radioactive gas radon was taken. An wider thick-walled glass-tube B, projecting upwards into a sealed capillary end tube C, surrounded A. The air from B and C was pumped out and the apparatus allowed to stand for a few days. The α-particles emitted from radon passed out through the thin walls of A and entered B. The gas volume in B was compressed by introducing mercury through a side-tube when α-particles accummulated in C. An electric discharge between two electrodes (already sealed in C) was passed and the spectrum of the discharge was identified to be that of Helium. This confirmed that α-particles were charged helium atoms.

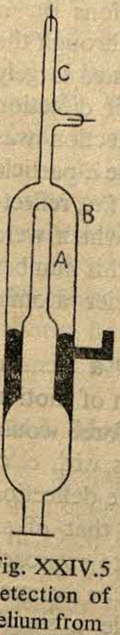


Fig. XXIV.5
Detection of
Helium from
α-particles

β-rays: (*i*) The β-rays consist of negatively charged particles as observed from their deflection in a given magnetic field.

(*ii*) Kaufmann measured the *e*/*m*-value of these particles and found the value to be the same as that of the electrons. The β-rays are really streaming electrons.

(*iii*) The β-particles have high velocities and often reach nearly 80% of that of light.

(*iv*) The β-particles have a higher penetrating power than that of the α-particles but less than that of the γ-rays.

γ-rays: The γ-rays have much greater penetrating power than α- or β-rays. The γ-rays can be detected even after passing through 30 cm. of iron. These rays are not deviated by a magnetic field and therefore carry no charge. In fact, the rays are electromagnetic waves of very short wavelengths ranging approximately between 4Å to 0.04Å. They are thus comparable to X-rays and differ from the latter only in respect of their origin. The γ-rays affect photographic plates and are capable of ionising gases though the effect is small. With an intense beam of γ-rays, phosphorescence on a fluorescent screen has also been observed.

24.7. Scattering of α-particles: Rutherford's atom

The presence of negatively charged electrons in atoms was confirmed. The atom as a whole being electrically neutral, there must exist within the atom positive charges. The emission of α-particles from radioactive atoms pointed to the possibility of existence of positively charge units within.

In 1909, at the instance of Rutherford, Geiger and Marsden studied the scattering of α-particles by passing them through thin metal sheets. A beam of α-rays was allowed to pass through a narrow hole and then to strike a thin metal foil, say a gold leaf. The direction of motion of α-particles after emerging from the metal sheet was traced by allowing them to produce scintillations on a fluorescent screen. It was noticed most of the particles passed straight through the metal or suffer very slight deflection. This suggested that matter consisted largely of emptiness. But a few of these α-particles (about 1 in 8000) changed their direction quite sharply; in some cases the deflection was more than 90°. Even in a few cases, the α-particle after the encounter moved backwards *i.e.*, reflected back. The number of α-particles which were strongly deflected, was not large, but this number increased with metal foils of heavier atomic weights (Fig XXIV.6).

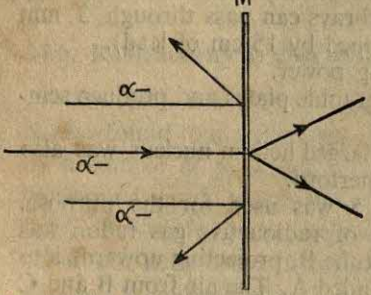


Fig. XXIV.6. Scattering of α-'particles from a gold foil (M)

The α-particles shoot out with a tremendous speed. To alter their direction of motion and reverse their path, enormous force would be needed. The impact of α-particles with electrons of the atom would not cause the deflection of the former, for, the mass of an α-particle is more than 7000 times that of an electron. For a scattering of more than 90°, the α-particle is required to approach a sufficiently heavy mass carrying a powerful positive charge. Even if it be assumed that the entire mass of the atom takes part in repelling the α-particle, a simple calculation with Coulomb's law shows that the α-particle must approach the charge within a distance of 10^{-12} cm. To explain the mechanism of the big deflections of the α-particles, it thus becomes necessary to presume the presence of positive charges concentrated within a volume of diameter less than 10^{-12} cm inside the atom. Moreover, practically the entire mass of the atom should also be concentrated within that volume. Only under these conditions, can an α-particle recoil or suffer large deflection (after colliding with a concentrated positive charge and a large mass). An impact of such type would be similar to the rebounding of a rubber ball from a big stone.

From these considerations, Rutherford was led to propose a nuclear theory for the structure of the atom (1911). The theory may be broadly summarised as follows:

(*i*) The atom consists of a very minute **nucleus** at its centre in which is concentrated practically the entire mass of the atom. The dimension of the nucleus is negligible compared to the radius of the atom. The radius of an atom is of the order of 10^{-8} cm and that of the nucleus $10^{-12} \sim 10^{-13}$ cm.

(*ii*) The entire positive charge also resides in the nucleus. The positive charge is Ze, where e is the unit charge equivalent in magnitude to that of an electron and Z is the number of such units of charge existing in the nucleus. The particle carrying a unit + *ve* charge was the *proton*.

(*iii*) Outside the nucleus there are Z electrons, so that the atom is ultimately neutral. These electrons are continuously moving around the nucleus with high speed. The arrangement is similar to that in the Solar system; the nucleus corresponds to the Sun and electrons to the revolving planets.

(*iv*) The number of positive charges (Z) in the nucleus is the *atomic number* of the element and really represents the ordinal number of the element in the periodic table. The number of electrons in the atom is also Z.

The atoms of all elements are structurally similar, they differ only in the number of positive charges in their nuclei. The fundamental identity of an element is its atomic number.

The series of atomic numbers, as shown by van der Broeck, reveals that successive atoms counting from hydrogen have nuclei containing one additional positive charge for each step in the atomic number.

A practical verification of the nuclear charge was made by Chadwick in 1920. By measuring the angle of deflection of the α-particle by the nuclei of some heavy atoms, he could establish the atomic number of the element.

A corroboration of this concept came from Moseley's experiments.

24.8. Moseley's Experiment: Atomic Number determination

It was known that when an element present in the anticathode was bombarded with cathode-ray electrons the X-rays emitted were characteristic of the elements. In 1913, the young English physicist Moseley investigated systematically the spectra of the X-rays emitted by different elements. He used anticathodes made of the element to be studied or coated them with one of its compounds. The X-rays emitted from these anticathodes were diffracted through a crystal of potassium ferrocyanide and the resulting rays were allowed to fall on a photographic plate.

From the relative positions in the photograph, the frequencies of the lines were determined.

The outstanding feature of the X-ray spectra was their simplicity and their great similarity to each other. In Fig. XXIV.7 are shown the lines in the X-ray spectra of some neighbouring elements of the periodic table from calcium to zinc.

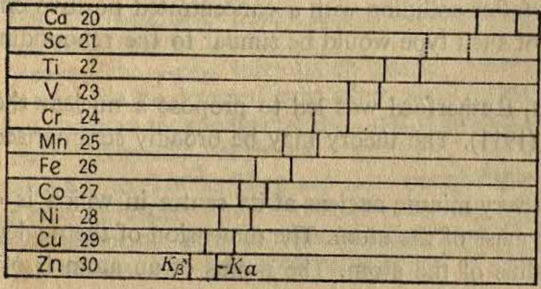


Fig. XXIV.7. X-ray spectra (K-series)

The characteristic spectrum of each element was found to consist of two lines, one being very prominent called the K_a-line. (In reality each of these two lines was closely spaced a doublet, *i.e.*, there were four lines). A glance at this picture would reveal that the characteristic frequency of a line, say K_a-line, changed regularly, from element to element, *i.e.*, with the ordinal number of the element in the periodic table. To pass from the spectrum of one element to that of the next, it was only necessary to shift the frequency to the left by a definite amount. In other words, there was a simple relation between frequency of the line and the position in the periodic table.

These lines were called the lines of the *K*-series. But when elements of comparatively heavier atomic weights were taken, a second series of characteristic lines were obtained on diffraction called the *L*-series lines. With heaviest atoms a third *M*-series lines were found.

By comparing the frequencies (ν) of the most prominent lines in the spectrum of a series, Moseley established a relation between the ordinal number (Z) of the element in the periodic table and the frequency ν which was given by the expression

$$\nu^{\frac{1}{2}} = a^{\frac{1}{2}}(Z-b) \qquad \ldots \text{(XXIV.1.)}$$

where a and b are constants. For the lines of the *K*-series, $a = 2.47 \times 10^{15}$ and $b = 1$, which predicts linearity between Z and $\sqrt{\nu}$. This was realised, as shown in Fig. XXIV.8. (See also p. 464).

That the ordinal number, *i.e.*, the atomic number (Z), is the fundamental characteristic of the element was obvious. Moseley's work immediately cleared two difficulties of the periodic table. There were instances where elements with higher atomic weight had to be placed earlier than the elements with lesser atomic weight, *e.g.*, Argon and Potassium, Tellurium and Iodine, etc. Such anomaly was removed when Moseley showed that atomic number of iodine was greater than that of tellurium though the atomic weights were not so. The same was the case with other anomalous pairs.

Again, from the blanks in the atomic number-frequency curves Moseley postulated that four elements of atomic numbers 43, 61, 72 and 75 remained to be discovered. These missing elements have since been discovered.

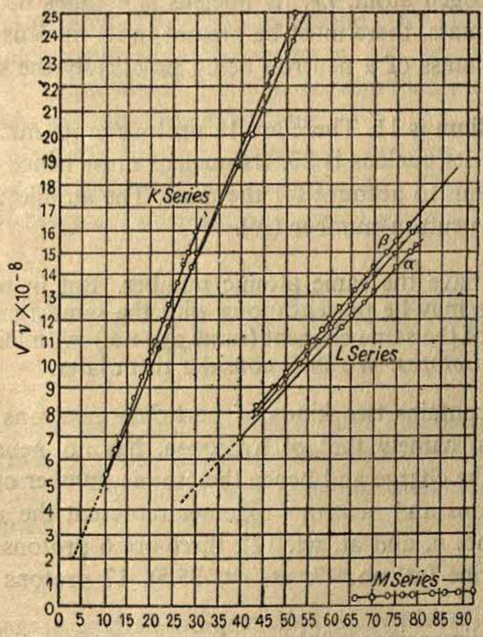


Fig. XXIV.8.

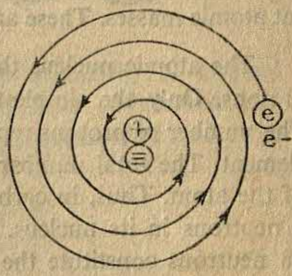


Fig. XXIV.9.

Drawbacks in the Rutherford's concept. The experimental confirmation of the Rutherford equation, the direct determination of nuclear charge by Chadwick, the fixation of atomic number from Moseley's X-ray spectra—all these lend strong support to Rutherford's concept of the atomic structure with a kernel of positively charged nucleus where the entire mass is concentrated surrounded by electrons moving in different orbits. And yet there remained two snags in the acceptance of this picture. (1) How could all the protons carrying positive charges be compressed together in the extremely minute nucleus without repulsion from one another? (2) In the orbital motion of the electrons, the inward attractive force was supposed to be counterbalanced by the outward centrifugal force. But electrons are charged particles. By the electromagnetic theory, the rotating electron should continuously emit energy as radiation during its motion. In consequence, the radius of its orbit would steadily diminish and the electrons would eventually fall into the nucleus. But this does not happen.

The Rutherford model also could not explain the enormous number of lines observed in the atomic spectra.

24.9. The Nucleus

When the only electron of a hydrogen atom is removed, the bare nucleus with a unit charge and a mass almost equal to that of a hydrogen atom is left. This is the *proton.* The proton is a fundamental particle of practically unit mass (amu) with a unit positive charge. The positive charge of the nucleus of the atoms of other elements consists of two or more protons. Thus, sodium (ordinal no. 11, *i.e.*, atomic number 11) has 11 units of positive charge or 11 protons in its nucleus.

But except for the ordinary hydrogen atom, the protons alone cannot account for the total mass of the atom (electron mass negligible). For example, helium (at. no. 2) nucleus has two protons, which accounts for 2 units of mass. But He-atom is 4 times as heavy as a hydrogen atom, *i.e.* its nucleus is 4 times heavier than a proton. To account for this mass, there must be present in its nucleus two neutrons along with 2 protons (the mass of a neutron being practically the same as that of a proton).

Similarly, the atomic no. of sodium is 11. There are 11 protons in its nucleus. But its atomic mass i.e. the mass of its nucleus is 23. Its nucleus must hence contain 12 neutrons along with 11 protons to account for the mass. The atomic mass units (A) = atomic number (Z) + neutron number (N).

A given element must always have the same atomic number. But in many cases, different numbers of neutrons may be present along with the same number of protons. This gives rise to atoms of the same element (same at. no.) with different atomic masses. These are called *isotopes*. We shall consider them later.

The atomic nucleus therefore contains two kinds of particles—neutrons and protons. Only the simplest nucleus, namely that of hydrogen, has no neutron. The number of protons represents the charge and hence the atomic number of the element. The total number of protons and neutrons together represent the mass of the atom. Thus, in carbon (at. no. 6, and at. wt. 12), there are 6 protons and 6 neutrons in its nucleus. In chlorine (at. no. 17, at. wt. 35.5), 17 protons and 18 neutrons constitute the nucleus.

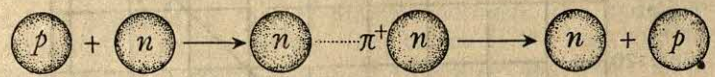
Stability of the Nucleus: The dimensions of the nucleus are extra-ordinarily small (its diameter is only $10^{-13} \sim 10^{-12}$ cm) compared with the dimensions of the atom (diam. 10^{-8} cm). An empirical relation for the radius (r) of the nucleus of an atom of atomic number (A) is given by

$$r = 1.2 \times 10^{-13} A^{1/3}$$

In that minute compass of the nucleus, all the protons and neutrons are clustered together. What holds the nucleus together? Normally the protons should repel one another because of their charge. There must then be some other force which overcomes the coulombian repulsion and provides stability. To explain this, Yukawa in 1935, proposed a theory which is now believed to be substantially correct. The particles—neutrons and protons—are held together by what is termed as *exchange force*. These forces are extremely short-range and in close proximities they outweigh the long-range electrostatic repulsion. So that when the dimension is of the order of 10^{-13} cm the attraction between proton—proton, neutron—proton or neutron—neutron is practically the same. In virtue of the exchange force there is a constant interchange, within the nucleus, between neutron—proton, proton—neutron or even between two protons or two neutrons. In fact, the particles, neutrons and protons, are regarded as the two different states of the same fundamental particle, now called *nucleon*. Yukawa further showed mathematically that such exchanges between neutron and proton would be possible only through a small intermediate particle, which was named a meson. That means two nucleons are held together through the sharing of a meson. The mesons are subatomic particles and are of different types; *e.g.*, μ-mesons (or muons) or π-mesons (or pions). These have extremely short lives and possess a mass $200 \sim 300$ times that of an electron.

It is now believed that each nucleon—proton or neutron—has a central core which is surrounded by a mesonic cloud. This cloud provides the π-mesons through which interchange of proton-neutron, etc. occurs. The mesons may be positive, negative or neutral $(\pi^+, \pi^-, \pi^\circ)$. A simplified picture of the interchange may be described along the following lines.

In a proton-neutron conversion, imagine a proton (p) release a π^+ meson and itself is converted into a neutron (n). The released π^+ meson adheres to the cloud of neutron transforming it into a proton. Thus



The net result is that though there has been a change in identity of original proton and neutron, the final state produces the same number of neutron and and proton and the energy remains unaltered. The transformation may be represented,

as
$$p + n \rightarrow [n' + \pi^+ + n] \rightarrow n' + p'$$

the prime is used to indicate the changed identity.

A similar exchange may take place through a negative pi-meson (π^-) or a neutral pi-meson (π°). And in each case, the number and type of nucleons remain unaltered without any change in energy.

(*A*) $n + p \rightarrow p' + \pi^- + p \rightarrow p' + n'$

(*B*) (*i*) $p + p \rightarrow p' + \pi^\circ + p \rightarrow p' + p'$

(*ii*) $n + n \rightarrow n' + \pi^\circ + n \rightarrow n' + n'$

The theory had its great support from the discovery of mesons from cosmic rays with similar mass and similar properties.

Qualitatively speaking, nuclear stability depends on the number of protons and neutrons present. For lighter elements (up to $Z = 20$) the most stable nuclei are found and the number of protons and neutrons in their nuclei are equal. In other words, their n/p ratio $= 1$; or $A/Z = 2$. In heavier elements, always there is a larger number of neutrons than protons. Increase in proton - number brings in higher degree of repulsion and hence instability. Excess neutrons counteracts the repulsion and stabilise the nuclei. The ratio n/p increases gradually up to 1.6 (Fig. XXIV. 8a). Above this value, the nucleus becomes very unstable and spontaneous radioactive disintegration takes place.

As mentioned earlier, Rutherford's model was inadequate on other counts; it could not explain why the revolving electrons would not ultimately fall on the nucleus and also it could not account for the innumerable discrete lines found in the atomic spectra. It was **Niels Bohr** who succeeded in solving the problem. Meantime Planck established his famous Quantum theory.

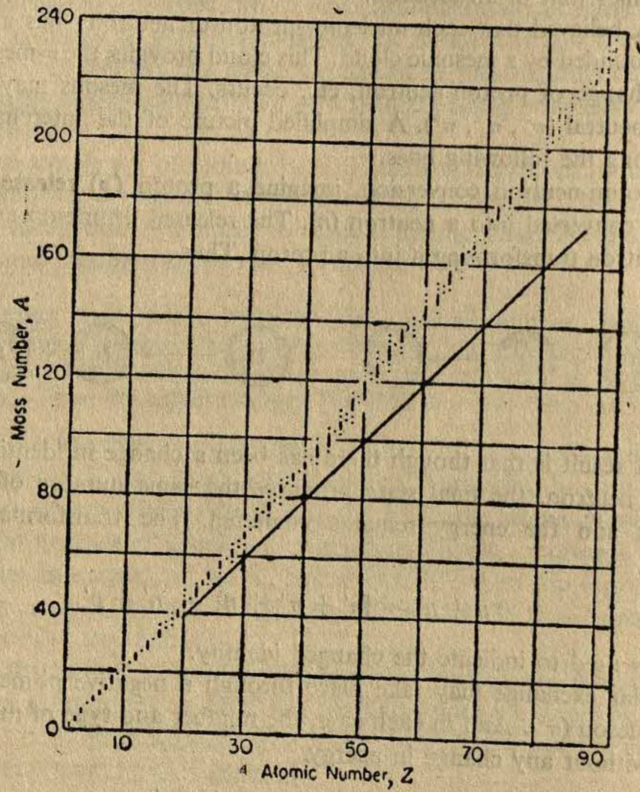


Fig. XXIV.8a. (*A vs Z*)

24.10. Planck's Quantum Theory

In 1901 Planck proposed a revolutionary hypothesis in which he discarded the precept that an oscillator emits or takes up energy *continuously* and suggested that energy changes occur in discrete amounts. Planck introduced three assumptions:

(*i*) the energy of an oscillator cannot vary continuously but only by discrete amounts. Hence an oscillator has definite energy levels, such as $\epsilon_0, \epsilon_1, \epsilon_2, \epsilon_3, \ldots \epsilon_i, \ldots$ etc.

(*ii*) the oscillator emitting a frequency ν can only radiate in units or *quanta* of the magnitude $h\nu$, where h is a fundamental constant of nature,

$$\epsilon = h\nu$$

This really amounts to introduction of the concept of atomicity in the realm of energy. The value of $h = 6.625 \times 10^{-27}$ erg-sec.

(*iii*) The energy levels of the oscillator can only be integral multiples of a quantum, *i.e.*,

$$E_n = n\epsilon = nh\nu$$

where n is an integer.

This, known as the Planck's Quantum Theory, profoundly altered the entire outlook of physics. It yielded the most satisfactory theory for black-body radiations and also explained clearly many other phenomena, such as the specific heat of solids, the atomic spectra, photoelectric effect, etc.

24.11. The atomic spectra

Probably the most important aid in determining the structure of an atom has been the study of radiation emitted and absorbed by the elements. The glowing atoms of an element emit radiations. These radiations, when dispersed through a suitable prism, are found to consist of a large number of lines which are characteristic of the element. The atoms of an element always produce line spectra, often called the *atomic spectra*. The atomic spectra of an element is usually very complex and their analysis is quite a difficult job. The simplest of the atomic spectra, as it is expected, is that of atomic hydrogen. The hydrogen spectrum has been extensively investigated; the frequencies of the lines and the relations between them have also been determined with great precision. This study has helped us to understand the structure of other atoms too.

The hydrogen line spectrum in the visible region consists of four lines (H_α, H_β, H_γ, H_δ) which gradually close up. In fact, these four lines are only a part of a series of lines, nearly thirty in number, extending into the ultraviolet region. As they proceed towards ultraviolet, the lines come closer and closer until these merge. A diagrammatic presentation of the lines is given in Fig. XXIV.10. The position of the lines in the spectra may be indicated in terms of wavelengths (λ) or more generally, in terms of wave number ($\bar{\nu}$), *i.e.*, the number of waves per unit length such that $\bar{\nu} = 1/\lambda$. Thus, the line H_β has $\lambda = 4861.3$ Å, *i.e.*, $\bar{\nu} = 20572 \text{ cm}^{-1}$.

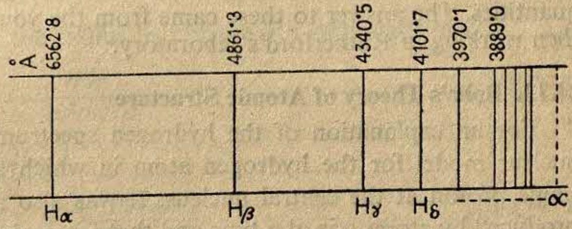


Fig. XXIV.10. Balmer Series

In 1885, Balmer discovered a relation between the wave-number ($\bar{\nu}$) and the position of the lines in the series, since then called the Balmer series. The relation is

$$\bar{\nu} = R\left[\frac{1}{2^2} - \frac{1}{n^2}\right]; \ (n = 3, 4, 5 \ldots) \qquad \ldots (i)$$

where R is a constant called Rydberg constant empirically found to be 109678 cm^{-1}; and 'n' is an integer having values of $n = 3, 4, 5, 6$, etc. With this value of R, and putting $n = 3, 4$, etc. it is possible to reproduce the entire Balmer series of lines.

The nature of this relation prompted Balmer and Ritz to realise that there might exist other series of spectral lines in which the first term in eqn. (i) would be different from $\frac{1}{2^2}$. In 1908, Ritz discovered the *principle of combination*, in which it was found that the wave-number of any line in a series would be the difference of two square terms, as

$$\bar{\nu} = R\left[\frac{1}{m^2} - \frac{1}{n^2}\right] \qquad \ldots (ii)$$

where R is the same Rydberg constant, and m and n are integers, such that $n > m$.

In fact, four other series have later been discovered in the entire spectrum of hydrogen all of which are governed by the relation (*ii*) mentioned above. In the ultraviolet region, Lyman series was soon found in which $m = 1$ and $n = 2, 3, 4,$

Lyman series : $$\bar{\nu} = R\left[\frac{1}{1^2} - \frac{1}{n^2}\right] \quad \ldots (iii)$$

Similarly in the near and far infra-red regions, three other series of lines have been observed:

$$\left.\begin{aligned} &\text{Paschen series :} \quad \bar{\nu} = R\left[\frac{1}{3^2} - \frac{1}{n^2}\right]; \; n = 4, 5, 6, \ldots \\ &\text{Brackett series :} \quad \bar{\nu} = R\left[\frac{1}{4^2} - \frac{1}{n^2}\right]; \; n = 5, 6, 7, \ldots \\ &\text{Pfund series :} \quad \bar{\nu} = R\left[\frac{1}{5^2} - \frac{1}{n^2}\right]; \; n = 6, 7, 8, \ldots \end{aligned}\right\} \quad \ldots (iv)$$

A theoretical basis to explain the formation of line spectra and its obedience to the Ritz principle was not obvious. We know that in the hydrogen atom, a single electron revolves in a circle round a proton as nucleus. According to classical mechanics, as the energy is radiated by the electron, the orbital radius must also change and ultimately the electron should fall into the nucleus. The energy should therefore be radiated in a continuum and the observed line spectra indicating discrete energy changes is not expected. The classical theory therefore cannot explain the formation of line spectra. Not only this, there remains the other question as to why the wave number of these lines are represented as the difference of two quantities. The answer to these came from the young Dane, Niels Bohr, who was then working in Rutherford's laboratory.

24.12. Bohr's Theory of Atomic Structure

For an explanation of the hydrogen spectrum, Bohr adopted Rutherford's nuclear model for the hydrogen atom in which an electron revolves round the single proton at the central nucleus. It was also accepted that spectral lines are produced by atoms one at a time and that for each line a single electron is responsible. Bohr then introduced two new postulates. These postulates appeared to be quite arbitrary at the time they were proposed but subsequently proved to be reasonably valid from wave-mechanical considerations. These two postulates are:

(*i*) The electron can revolve round the nucleus in only some definite orbits. The permissible orbits are those for which the angular momentum of the electron is an integral multiple of $h/2\pi$. These are termed stationary orbits and no energy is radiated when the electron revolves in a stationary orbit.

The angular momentum, $mvr = nh/2\pi$, where n is an integer called the quantum number indicating the energy level.

(*ii*) During the emission or absorption of radiant energy, the Planck-Einstein equation, $\epsilon = h\nu$ is obeyed. That is, radiant energy is emitted or absorbed in whole quanta $h\nu$. If E_i and E_f be the initial and final energy levels during emission or absorption of energy, then

$$h\nu = E_i \sim E_f$$

where ν is the frequency of the radiation. It is obvious radiation will be emitted only when an electron will jump from a stationary orbit of higher energy to one of lower energy.

Now consider an electron moving in the nth orbit at a distance r from the nucleus of charge Ze, Z being the atomic number. We know, its angular momentum,

$$mvr = \frac{nh}{2\pi} \qquad \ldots (i)$$

The electrostatic force on the electron is $\frac{Ze.e}{r^2}$ and the centrifugal force is $\frac{mv^2}{r}$ and these must balance one another in a stationary orbit. Hence,

$$\frac{mv^2}{r} = \frac{Ze^2}{r^2} \qquad \ldots (ii)$$

i.e., the kinetic energy, $E_k = \frac{1}{2}mv^2 = \frac{Ze^2}{2r} \qquad \ldots (iii)$

The potential at a distance r from the central charge Ze is given by $\frac{Ze}{r}$.

Hence, its potential energy, $E_p = -\frac{Ze^2}{r} \qquad \ldots (iv)$

The total energy, of the electron at the nth orbit (E_n), would be,

$$E_n = E_k + E_p = \frac{Ze^2}{2r} - \frac{Ze^2}{r} = -\frac{Ze^2}{2r} \qquad \ldots \text{(XXIV.2)}$$

Eliminating v from (i) and (ii), the radius (r_n) of the nth stationary orbit,

$$r_n = \frac{n^2h^2}{4\pi^2me^2Z} \qquad \ldots \text{(XXIV.3)}$$

Substituting this in eqn. (XXIV.2),

$$E_n = -\frac{2\pi^2me^4Z^2}{n^2h^2} \qquad \ldots \text{(XXIV.4)}$$

For H-atom,

$$r_n = \frac{n^2h^2}{4\pi^2me^2Z} = \frac{n^2h^2}{4\pi^2me^2} \quad (\text{since } Z = 1) \qquad \ldots \text{(XXIV.5)}$$

For the permissible stationary orbit nearest to the nucleus, $n = 1$. Hence the radius of the 1st Bohr orbit will be

$$r_1 = \frac{h^2}{4\pi^2me^2} = (6.625 \times 10^{-27})^2/[4 \times (3.14)^2(4.8 \times 10^{-10})^2 \times 9.11 \times 10^{-28}]$$

$$= 0.529 \text{ Å}$$

using the standard values of m, e and h, available from other sources. This value is nearly the same as the one obtained from the kinetic theory considerations. The radius of any other orbit of quantum number n will be given by

$$r_n = n^2 . \frac{h^2}{4\pi^2e^2m} = n^2r_1 \qquad \ldots \text{(XXIV.6)}$$

From eqn. (XXIV.4) the energy of the electron in the nth and n'th stationary orbit would be

$$E_n = \frac{-2\pi^2me^4}{n^2h^2} \quad \text{and} \quad E_{n'} = \frac{-2\pi^2me^4}{n'^2h^2}$$

when an electron jumps from the nth level to the n'th level, where $n > n'$, the energy emitted in the form of radiation of, say, frequency ν is

$$h\nu = \frac{-2\pi^2me^4}{h^2}\left[\frac{1}{n^2} - \frac{1}{n'^2}\right]$$

or

$$\nu = \frac{2\pi^2me^4}{h^3}\left[\frac{1}{n'^2} - \frac{1}{n^2}\right] \qquad \ldots \text{(XXIV.7)}$$

The corresponding wave-number ($\bar{\nu}$) of the radiation shall be

$$\bar{\nu} = \frac{2\pi^2me^4}{ch^3}\left[\frac{1}{n'^2} - \frac{1}{n^2}\right] \qquad \ldots \text{(XXIV.8)}$$

The empirical relation derived from Balmer series lines, and also from Lyman and other series for the wave number is

$$\bar{\nu} = R\left[\frac{1}{m^2} - \frac{1}{n^2}\right]$$

Comparing, R is found to be equal to $2\pi^2me^4/ch^3$,

$$\textit{i.e.,}\quad R = \frac{2\pi^2me^4}{ch^3} = \frac{2(3.142)^2(9.108\times10^{-28})(4.8\times10^{-10})^4}{(3\times10^{10})(6.625\times10^{-27})^3} = 109737\ \text{cm}^{-1} \qquad \ldots \text{(XXIV.9)}$$

putting the standard values of m, e, c and h.

This excellent agreement of the value of R with the experimental result is indeed a very strong support of the Bohr's theory. The accuracy of this relation becomes more obvious when the frequencies or wavelengths of the emitted radiations calculated with eqn. (XXIV.7) are compared with the experimental values. For example, in Balmer series, $n = 2$; we have,

BALMER LINES IN ATOMIC HYDROGEN SPECTRUM

n'	λ(calc.)	λ(expt.)
3	6562.89	6562.8
4	4861.38	4861.4
5	4340.51	4340.5
6	4101.78	4101.8

The electron in the hydrogen atom, according to the Bohr's theory, will be in one of the circular orbits around the nucleus; the orbits are characterised by the **quantum numbers,** $n = 1, 2, 3, 4$, , , etc. No energy emission occurs as long as the electron remains in a stationary orbit. But whenever the electron jumps from an outer to an inner orbit, energy is emitted, Thus, whenever an electron jumps down to the orbit $n = 2$ from any outer orbit $n = 3, 4, 5 \ldots$, the lines in the Balmer series are obtained. The line H_α in the Balmer series is due to the transition of an electron from the orbit $n = 3$ to the orbit $n = 2$.

On the other hand, a transition of the electron from orbit $n = 4$ to orbit $n = 3$ will produce a line of the Paschen series in the infra-red. If the electron jumps from orbit $n = 4$ to orbit $n = 1$, it will give rise to a line in Lyman series. In other words, Lyman, Balmer, Paschen, Bracket and Pfund series are formed when electrons jump to orbits $n = 1, 2, 3, 4$ and 5 respectively from outer orbits. This is illustrated in Fig. XXIV. 11.

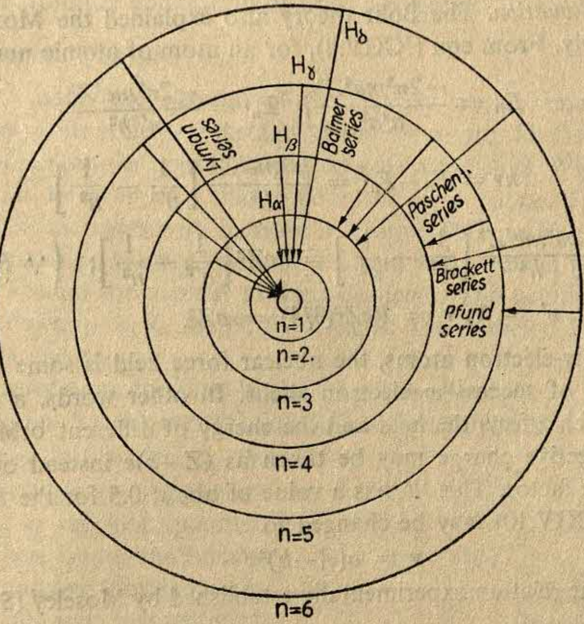


Fig. XXIV.11. Diagrammatic presentation of Bohr orbits of hydrogen atom

Example 1. Calculate the velocity and kinetic energy of the electron in the ground state ($n = 1$) of the H-atom.

From eqn (*i*), Sec 24-12, $v = nh/2\pi mr$

Substituting appropriate values,

$$v = \frac{1 \times 6.6256 \times 10^{-27}}{2(3.14)\,(9.1 \times 10^{-28})\ (0.529 \times 10^{-8})} = 2.188 \times 10^{8} \text{ cm/sec.}$$

The kinetic energy,

$$E = \frac{-2\pi^2 Z^2 e^4 m}{n^2 h^2}, \quad \text{(eqn. XXIV. 4)}$$

$$= \frac{-2(3.14)^2 \times (1)^2\,(9.10 \times 10^{-28})\,(8.4803 \times 10^{-10})^4}{(1)^2 \times (6.6256 \times 10^{-27})^2}$$

$$= -2.179 \times 10^{-11} \text{ ergs} = -313.3 \text{ kcal.}$$

Example 2. Calculate the Bohr radius for the 2nd orbit of the hydrogen atom. For the 1st orbit,

$$r_1 = \frac{n^2h^2}{4\pi^2Ze^2m} = \frac{h^2}{4\pi^2Ze^2m} = 0.529\text{Å}$$

For the second orbit ($n = 2$),

$$r_2 = \frac{4.h^2}{4\pi^2ze^2m} = 4\times 0.529\text{Å}$$

$$= 2.116\text{ Å}$$

Moseley's Equation. The Bohr theory also explained the Moseley's equation very satisfactorily. From eqn (XXIV.4), for an atom of atomic number Z,

$$E_n = \frac{-2\pi^2me^4Z^2}{n^2h^2}, \quad E_{n'} = \frac{-2\pi^2me^4Z^2}{n'^2h^2}$$

Hence, $$h\nu = E_n - E_{n'} = \frac{2\pi^2me^4Z^2}{h^2}\left[\frac{1}{n'^2} - \frac{1}{n^2}\right]$$

or $$\nu = \frac{2\pi^2me^4Z^2}{h^3}\left[\frac{1}{n'^2} - \frac{1}{n^2}\right] = RcZ^2\left[\frac{1}{n'^2} - \frac{1}{n^2}\right]; \quad \left(\because R = \frac{2\pi^2me^4}{ch^3}\right)$$

When $n = 2$, $n' = 1$; $\nu = RcZ^2(3/4) = aZ^2$ ...(XXIV.10)

Now, in poly-electron atoms, the nuclear force field is some what influenced by the presence of successive electron shells. In other words, a screening effect is produced which affects the field and the energy of different orbits is somewhat altered. The effective charge may be taken as $(Z-b)e$ instead of Ze, where 'b' is the correction factor. This 'b' has a value of about 0.5 for the K-radiation. So, the equation (XXIV.10) may be changed to

$$\nu = a(Z-b)^2$$

This indeed is the relation experimentally established by Moseley (Sec. 24.8).

Example 3. The wavelengths of K_α characteristic X-ray of iron and potassium are 1.931×10^{-8} and 3.737×10^{-8} cm respectively. What is the atomic number and name of the element for which K_α wavelength is 2.289×10^{-8} cm? (Pune B.Sc.).

Suppose Z_1, Z_2 and Z_3 are the atomic numbers of Fe, K and the unknown element. From equation (XXIV.10),

$$Z^2 \propto \nu \propto \frac{C}{\lambda}, \text{ where } \lambda \text{ is the wavelength.}$$

Hence $$\frac{Z_3^2}{Z_1^2} = \frac{\lambda_1}{\lambda_3}; \quad \text{or} \quad Z_3^2 = \frac{\lambda_{\text{Fe}}}{\lambda_3} \times Z_1^2$$

where λ_3 is the wavelength for the unknown element.

Now $Z_1 = 26$; $$\therefore \quad Z_3^2 = \frac{1.931}{2.289} \times 26^2 = 570.7$$

or $$Z_3 \approx 23.9$$

Again $Z_2 = 19$; $$Z_3^2 = \frac{\lambda_K}{\lambda_3} \times Z_2^2 = \frac{3.737}{2.289} \times 19^2 = 590$$

whence $Z_3 \approx 24.1$

∴ The atomic number is 24; the element is chromium.

Limitations of Bohr's Theory: (*i*) The Bohr theory certainly made an achievement by producing a pictorial representation of the hydrogen atom, which explained the atomic spectral data. But attempts to apply this theory to atoms with more than one electron were not successful. (*ii*) The theory did not provide any explanation for the union of atoms to produce molecules. (*iii*) The Bohr theory also did not recognise the wave property of the electron which was subsequently established by de Broglie (1923). (*iv*) The Bohr theory also could not account for the splitting of lines of atomic spectra into group of finer lines when placed in a magnetic or an electric field (Zeeman and Stark effects). A modification of the Bohr's theory was first made by Sommerfeld and subsequently a more satisfactory explanation came from the application of wave mechanics.

24.13. Bohr-Sommerfeld Theory

According to Bohr, the electron of the H-atom could remain only in the circular stationary orbits at definite distances from the centre. The 1st orbit ($n = 1$) is at a distance of 0.529Å or approximately 53 pm (picometer). When the electron is in the nearest *i.e.* 1st orbit, it is said to be in the *ground state*. The energy associated with an orbit increases with increase in radius. These orbits are also called 1st, 2nd, 3rd . . . *quantum levels*. Generally it is said that electron (s) would occur in definite shells around the nucleus at fixed distances. The quantum levels from the nearest are known as *K*, *L*, *M*, *N*, *O*, *P* shells. The *K*-shell corresponds to the 1st quantum level and so on.

Under high resolution, the lines in the atomic spectra split up into groups of finer lines. To account for this multiplicity, Sommerfeld modified the Bohr's model by introducing elliptical orbits in the second, third and higher quantum levels. He proposed that in the first quantum level (or *K* shell) there is only the circular orbit. For the second and third quantum levels there are one and two elliptical orbits in addition to the circular orbit. In elliptical orbits, the nucleus is at one of the principal foci of the ellipse. In the second and higher quantum levels, the electron may be in the circular or in the elliptical orbits. This will entail a *small* variation in its energy value. Sommerfeld's orbits are illustrated in Fig. XXIV.12. This small difference in energy-values gives rise to fine-structures in the atomic spectrum. A quantum level is thus subdivided into 2 or more sublevels, or a shell would consist of several subshells. The average energy of these sublevels would be very close to the energy of the quantum level (n).

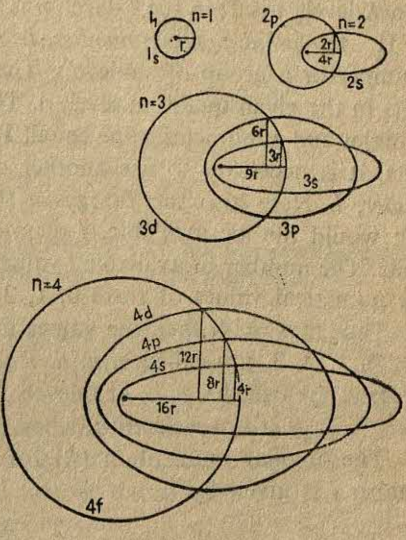


Fig. XXIV.12. Permitted electronic orbits of H-atom

When the electron moves in an elliptical orbit, its position and velocity continuously changes depending on the major axis and the angle between the radius and the axis. In Bohr's model, the presence of the electron could be defined only by n, the *principal quantum number*, but now the definition would require another quantum number l, called the *azimuthal quantum number*. In fact, l determines the ellipticity or shape of the orbit.

24.14. Quantum Numbers

There are four different quantum numbers for an electron in an atom. These quantum numbers enable us to understand the fine structures of the atomic spectra.

I. *Principal quantum number, n.* The electron, broadly speaking, can only exist in some well defined stationary orbits (Bohr) where its average energy would also be fixed. These orbits are numbered 1, 2, 3, . . ., commencing from that nearest to the nucleus. These are named quantum levels (K, L, M, N . . .) with quantum numbers $n = 1, 2, 3, \ldots$, This is the principal quantum number (n) to indicate in which level the electron exists.

The angular momentum in the case of an electron with quantum number (n) is.

$$m_e vr = n.\frac{h}{2\pi}$$

Again, the principal quantum number (n) enables us to ascertain the maximum number of electrons (N) which could be accommodated in that quantum level. The relation is $N = 2n^2$

So in K-level, n is 2; in the L-level, n is 8 ; in the M-level, n is 18; and so on.

II. *Azimuthal quantum number, l.* A Bohr quantum level is really made up of a number or a group of sublevels. The electron may revolve in various elliptical orbits in the given quantum level, n. The circle is a special case of an ellipse with the major and minor axes being equal. To define in which elliptical orbit the electron exists, it is necessary to use another quantum number called *azimuthal quantum number, l.* Here also the energy in the sublevels are quantised. Any elliptical path would not be available. l denotes the ellipticity and shape of the desired orbits. The number of available l-values for a given quantum number (n) is also n. The numerical values of l are 0, 1, 2, 3, . . ., $(n-1)$.

Thus if $n = 4$, then the values of l are 0, 1, 2, and 3. The electrons having $l = 0, 1, 2, 3$, are called *s*, *p*, *d*, *f* electrons respectively and the corresponding sublevels are called *s*, *p*, *d*, *f* sublevels. The electron having $l = 0$ is an *s*-electron. When $l = 1$, it is a *p*-electron; when $l = 2$ it is a *d*-electron and so on.

The angular momentum (L) for the electron with the azimuthal quantum number l is given by

$$L = \sqrt{l(l+1)}.\frac{h}{2\pi}$$

III. *Magnetic quantum number, m_l.* Zeeman observed that on the application of a magnetic field, the lines in the atomic spectra split up into groups of multiplets. The sommerfeld elliptical orbits were also taken as planar. The electron magnetic moment is parallel to the angular momentum and both of them are perpendicular to the plane of the orbit. On the application of the magnetic field, the angular momentum may point in any direction. But Stern and Gerlach showed that the angular momentum would have only some definite directions with respect to the magnetic field and cannot take any arbitrary direction. It means that electron orbit is limited to certain definite planes. In other words, it is quantised in space and hence often mentioned as *space quantisation.* It is obvious that the available directions in space have to be defined by an additional quantum number. It is called *magnetic quantum number,* denoted by m_l.

For a given value of l for an electron, the permitted values of magnetic quantum numbers are

$$l, (l-1), (l-2), \ldots\ldots, 0, \ldots\ldots -(l-1), -l.$$

That is there would be $(2l+1)$ magnetic quantum numbers.

Thus if $l = 2$, then

$$m_l = 2,\ 1,\ 0,\ -1,\ -2 \text{ (five possible values)}$$

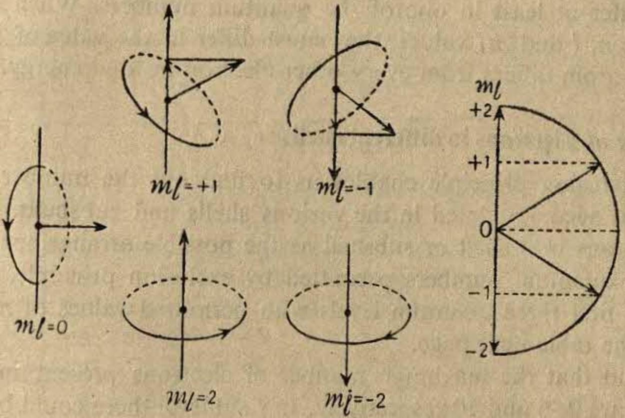


Fig. XXIV.13. Planes of magnetic quantum number ($l = 2$). The m_l-values indicate the tilt of the orbits with respect to the direction of the magnetic field

IV. *Spin quantum number, s.* While moving in its orbit, the electron also rotates on its own axis. This rotation may be clockwise or anticlockwise. An electron having the same three quantum numbers (n, l and m_l) may have a clockwise or anticlockwise spin. This would lead to slightly different net-energy values for the electron. This is why a line in the spectra appears as a doublet. For this spin, the electron is given an additional quantum number called *spin quantum number* denoted by s. Two values $+\frac{1}{2}$ and $-\frac{1}{2}$ are assigned to s, the spin quantum number. These values differ by unity. The spins are expressed with arrows ↑ or ↓ while writing. Two electrons having the same sign of the spin quantum numbers are said to have *parallel spins.* When two electrons have opposite signs for their spins, they are said to be *antiparallel or paired up spins* denoted as ⇅.

It is thus seen that an electron can be fully defined for its position and energy by four quantum numbers, n, l, m_l and s. It is seen that n gives the dimension of the orbit, l gives its shape, m_l gives the disposition of the orbit in space and s, the spin of the electron.

Example 4: Calculate the orbital angular momentum for $l = 3$.

We know, orbital angular momentum, $L = \sqrt{l(l+1)}. \frac{h}{2\pi}$.

Now $h/2\pi = 1.0545 \times 10^{-27}$ erg-second

$\therefore L = \sqrt{12} \times 1.0545 \times 10^{-27} = 3.65 \times 10^{-27}$ erg-sec.

24.15. Pauli's Exclusion Principle

From a searching scrutiny of the line spectra, Pauli put forward a very important principle which states:

"*No two electrons in an atom can have the same set of four quantum numbers.*"

This is known as the '*Pauli's exclusion principle*'. Any two electrons in an atom must differ at least in one of the quantum numbers. When two electrons have the same n, l and m_l values, they must differ in the value of s. Thus every electron in an atom differs from every other electron in total energy.

24.16. Number of Electrons in different shells

Pauli's exclusion principle enables us to find out the number of electrons which could be accommodated in the various shells and subshells. There can be as many electrons in a shell or subshell as the possible arrangement of electrons with different quantum numbers permitted by exclusion principle. The arrangements for the first three quantum levels with permitted values of n, l, m_l and s are given in the table next page.

It is found that the maximum number of electrons present in $s-$, $p-$ and $d-$ sublevels are 2, 6 and 10 respectively. In f sublevel there could be 14 electrons in the maximum. The largest possible number of electrons in different quantum levels are 2 for K-level, 8 for L-level, 18 for M-level etc.

Even with the acceptance of the elliptical orbits and the different quantum numbers, Sommerfeld theory could not be satisfatorily applied to polyelectronic atoms. A much better picture of the structure of an atom is available from consideration of wave-mechanical principles.

24.17. Wave-Particle Duality in Matter

Since the beginning of this century both the wave nature and the atomistic nature are accepted for radiations. In the phenomena of interference and diffraction the radiations are regarded as waves where as the photoelectric effect, Compton effect, etc. are explainable only in terms of quanta of radiations.

According to Louis de Broglie (1923), this dual nature—wave and particle—should not be confined to radiations alone but should also be extended to matter. He suggested that electrons, protons, atoms, etc. could not be regarded simply as corpuscles but that periodicity of wave motion must also be assigned to them.

TABLE : ASSIGNMENT OF ELECTRONS IN SHELLS

Shell	*Quantum numbers*				*Subshell*	*No. of electrons in Subshell*	*No. of electrons in completed shell*
	n	l	m_l	s			
K	1	0	0	$+\frac{1}{2}$	s	2	2
	1	0	0	$-\frac{1}{2}$			
L	2	0	0	$+\frac{1}{2}$	s	2	8
	2	0	0	$-\frac{1}{2}$			
	2	1	−1	$+\frac{1}{2}$	p	6	
	2	1	−1	$-\frac{1}{2}$			
	2	1	0	$+\frac{1}{2}$			
	2	1	0	$-\frac{1}{2}$			
	2	1	1	$+\frac{1}{2}$			
	2	1	1	$-\frac{1}{2}$			
M	3	0	0	$+\frac{1}{2}$	s	2	18
	3	0	0	$-\frac{1}{2}$			
	3	1	−1	$+\frac{1}{2}$	p	6	
	3	1	−1	$-\frac{1}{2}$			
	3	1	0	$+\frac{1}{2}$			
	3	1	0	$-\frac{1}{2}$			
	3	1	1	$+\frac{1}{2}$			
	3	1	1	$-\frac{1}{2}$			
	3	2	−2	$+\frac{1}{2}$	d	10	
	3	2	−2	$-\frac{1}{2}$			
	3	2	−1	$+\frac{1}{2}$			
	3	2	−1	$-\frac{1}{2}$			
	3	2	0	$+\frac{1}{2}$			
	3	2	0	$-\frac{1}{2}$			
	3	2	1	$+\frac{1}{2}$			
	3	2	1	$-\frac{1}{2}$			
	3	2	2	$+\frac{1}{2}$			
	3	2	2	$-\frac{1}{2}$			

de Broglie was led to this hypothesis from consideration of quantum theory and the special theory of relativity. He also proposed a relation between momentum and wavelength of a particle in motion. In considering light of frequency ν, the energy is given by $\epsilon = h\nu = h.\frac{c}{\lambda}$; ($\lambda$ = wave length, c = velocity of light). Again, from the theory or relativity, $\epsilon = mc^2$, (m = mass of photon).

Combining these two relations, $mc = h/\lambda$

or the momentum, $p = \frac{h}{\lambda}$, *i.e.*, $\lambda = \frac{h}{p}$; (h, Planck's constant) de Broglie extended this relation into the dynamics of a particle and proposed that a wavelength λ is associated with a particle in motion, which is related to its momentum as

$$\lambda = \frac{h}{p} = \frac{h}{mv} \quad \ldots (a)$$

where m is the total mass of the particle and v its velocity.

The velocity v (a particle property) is thus connected to wavelength λ (a wave property) by Planck's constant h. The validity of this hypothesis, *i.e.*, the existence of waves associated with particles, was demonstrated experimentally by Davisson & Germer (1927) and by G. P. Thomson (1928).

Thomson led a cathode ray beam (electrons) through a very thin foil of metal and allowed them to fall on a photographic plate. On development of the plate, a dark central spot surrounded by concentric rings was obtained (Fig. XXIV.14). It was clear that the electrons were diffracted by the metal atoms present in the crystal-lattice of the foil. The measurement of the wavelength corresponded to that predicted by de Broglie equation.

The wave-lengths of waves associated with a moving matter [eqn. (*a*)] are called *de Broglie wave-lengths*. These are significant only in the case of very small particles like electrons. Large particles in motion also have waves associated with them but their wave-lengths are not measurable or detectable. For example:

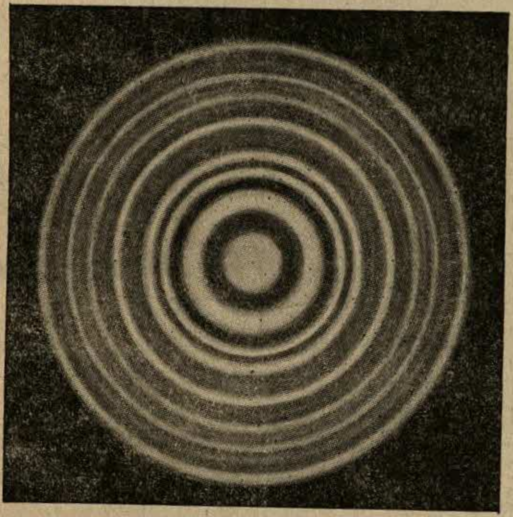


Fig. XXIV.14. Electron diffraction.

(*i*) Consider an electron in the 1st orbit of a hydrogen atom. Its wave-length

$$\lambda = \frac{h}{mv} = \frac{6.6256 \times 10^{-27}}{(9.109 \times 10^{-28})(2.188 \times 10^{8})}$$

$$= 2.46 \times 10^{-8} \text{ cm.}$$

This value is in the region of X-ray waves and hence can be detected.

(*ii*) Next imagine a 10-gm marble is moving with a velocity of 100 cm/sec. The de Broglie wave-length would be

$$\lambda = \frac{h}{mv} = \frac{6.6256 \times 10^{-27}}{10 \times 100} = 6.6256 \times 10^{-30} \text{ cm}$$

This small quantity is beyond detection by any means.

Bohr considered that the electron moves in circular orbits. By de Broglie's hypothesis, the moving electron has waves associated with it. For a stationary orbit, there should be a standing wave. It is necessary that the orbit-path must be an integral multiple of wave-lengths (Fig. XXIV.15). It means

$$2\pi r = n\lambda$$

where n is an integer.

$$\text{or} \quad 2\pi r = n\frac{h}{mv}$$

$$\text{i.e. } mvr = n\frac{h}{2\pi}$$

where mvr = angular momentum.

This is indeed the postulate Bohr assumed. Hence, de Broglie waves supports the Bohr's theory.

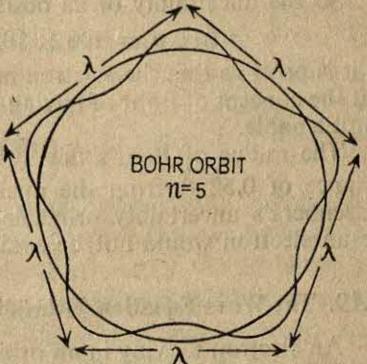


Fig. XXIV.15

24.18. The Uncertainty Principle

This principle, one of the fundamentals in modern physics, was propounded by Heisenberg. It states that *at any given instant it is not possible to determine simultaneously the exact position and the exact momentum of a particle.*

Consider a moving electron. Its position at any given moment cannot be seen with visible light as their wavelengths are more than million times larger then the size of the electron. Its position can be located by using X-rays. The diameter of the electron has nearly the same size as the X-ray wavelengths. But the interaction of the X-rays with the electron would cause Compton effect and the motion of the electron would be much accelerated. The velocity or the momentum of the electron would be quite uncertain though the position might be detected.

Again an electron diffracting through a metal foil may have its momentum correctly ascertained by using known fields. But on diffraction it is uncertain as to where the electron-wave would strike the photo-plate to produce the diffraction rings. That is, its position cannot be definitely ascertained.

Heisenberg also expressed the extent of the uncertainties quantitatively by the relation,

$$\triangle p . \triangle q \geqslant h, \text{ (Planck's constant)}$$

where $\triangle p$ is the uncertainty in momentum and $\triangle q$ that in its position. By rewriting,

$$\triangle v . \triangle q \geqslant \frac{h}{m}$$

where v and m are the velocity and mass of the particle.

If m is relatively large, say a ball of 1 gm, then the uncertainty ($\triangle p . \triangle q \approx h$, a small quantity) is almost nil. That is, the principle is not significant for large particles. Here we can find out both position and momentum simultaneously.

But for atomic and sub-atomic particles, this relation is quite important. For the electrons in Bohr's first orbit, the momentum (p) is

$$p = mv = (9.1 \times 10^{-28})(2.2 \times 10^{8}) = 2 \times 10^{-19} \text{ gm-cm/sec.}$$

Even if there is an uncertainty of only 1%, then $\triangle p = 2 \times 10^{-21}$

So the uncertainty of its position.

$$\triangle q = h/\triangle p = 6.6 \times 10^{-27}/2 \times 10^{-21} = 3.3 \times 10^{-6} = 330\text{Å}$$

So it is possible that the electron may be quite outside the atom itself. It suggests that the concept of Bohr of having the electron particle revolving at a fixed distance is not tenable.

The radius of Bohr's first orbit is fixed and the electron moves always at a distance of 0.529Å from the nucleus and its velocity is definite. According to Heisenberg's uncertainty principle, such precise values for velocity and position for an electron would not be available.

24.19. The Wave Equation (Schrödinger)

An electron moving in an orbit of the atom have a de Broglie wave associated with it. Since the path in the closed orbit is fixed, there would be an integral number of wavelengths for the stationary wave. It means that the electron would possess only those energy values which correspond to the permitted wavelengths or frequencies. For orbits in different quantum levels the frequencies would change. Hence, it has to be accepted that there are discrete energy levels for the moving electron and for the atom.

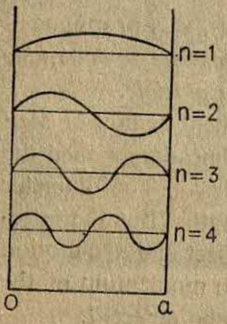


Fig. XXIV.16

A one dimensional wave motion, say, that of a vibrating string fixed at both ends is shown in Fig. XXIV.16. The different modes of vibration are integral multiples of the fundamental frequency (ν_0); so that $\nu_n = n\nu_0$, where $n = 1, 2, 3, 4 \ldots$ stands for quantum numbers corresponding to the permitted energy levels.

The displacement A at a point (x, y, z) at time t of a wave of frequency ν is given by

$$A = \psi \operatorname{Sin} 2\pi\nu t \qquad \ldots \text{(A)}$$

where ψ, called *wave function*, is the amplitude of the wave at the given point.

The standard equation for the propagation of elastic waves (along x-direction)

$$\frac{\partial^2 w}{\partial x^2} = \frac{1}{u^2} \cdot \frac{d^2 w}{dt} \qquad \ldots \text{(B)}$$

Using equations (A) and (B) and applying de Broglie equation, Schrödinger deduced the relation for the particle waves as

$$\frac{\partial^2 \psi}{\partial x^2} + \frac{\partial^2 \psi}{\partial y^2} + \frac{\partial^2 \psi}{\partial z^2} + \frac{8\pi^2 m}{h^2}(E-V)\psi = 0 \qquad \ldots \text{(XXIV.11)}$$

where E = total energy and V = the potential energy of a particle of mass m and h is Planck's constant.

In equation (A) above, only those values of ψ would be acceptable which satisfy the condition for a stationary wave ($\nu_n = n\nu_0$). Hence for certain definite values of energy (E), called *eigenvalues*, the solutions of ψ from equation XXIV.11 are acceptable. These energy values are equivalent to the discrete energy levels of Bohr model.

24-20. Interpretation of ψ : Orbitals

The concentric rings observed in the diffraction of electron beams through a metal foil indicate that more electrons strike at certain points (rings) than at other points. The electrons scarcely arrive in between the rings. It means, on diffraction an electron has a much higher *probability* in landing on one of the rings. These rings are places of higher electron density.

In the theory of propagation of light waves, the intensity of the light at any point is proportional to the square of the displacement of the wave at the point. Considered from the view-point of photons, the intensity should be proportional to the number of photons arriving at the point per second. But this number density of the photons is a measure of the probability of the occurrence of photons at the given point. We can therefore say that the probability of the occurrence of photons in a region is proportional to ψ^2, the square of the wave amplitude of a wave equation. It is not necessary to consider the trajectory the photons pursued to arrive at the spot.

Extending this idea to electron beams, the probability of an electron being found at a given small volume is proportional to $\psi^2 dv$, where ψ is the displacement function of the associated de Broglie waves at the spot of small volume dv. The wave function ψ of Schrödinger equation is thus a state function, the square of which (ψ^2) has a physical meaning related to probability. The purpose of the wave equation thus seems to be to provide statistical information about the place where the electrons are likely to be detected. Schrödinger adduced a physical significance to ψ^2, assuming that $\psi^2 dv$ would denote the charge density of the electrons in an atom within the region dv. That is, the electron is to be regarded as 'smeared out' into a cloud of electricity having different densities at different points.

Thus ψ^2 is the probability of expecting an electron at a given point. The wave function ψ is accepted for some definite energy levels which are found to be the same as the Bohr's quantum levels. Hence the wave functions ψ in the wave theory are the equivalents of Bohr's orbits. The wave functions (ψ) are usually called **Orbitals**. The wave theory rejects the idea of the electron particle being present at a particular point. The probability of its existence in a certain small volume is all that is known. It is not possible to define an exact path for its motion as in Bohr-Sommerfeld model. Physically speaking, the volume in space around the nucleus where there is maximum probability of its existence is called the 'orbital'.

As described earlier, an orbital has also four quantum numbers: the *principal*, the *azimuthal*, the *magnetic* and the *spin quantum numbers*.

The principal quantum numbers (n) denote the accepted energy levels of the wave function ψ and also the location (or size). As n increases, the energy levels recede from the nucleus and their values increase. The principal quantum numbers are the same as in Bohr's model. n is indeed a measure of the volume of the electron cloud.

The second quantum number is the *azimuthal quantum number* (l). It is also called the *orbital angular momentum quantum number*. The l-quantum numbers describe the geometrical shape of the orbital or the wave function. l is related to n, having values.

$l = 0, 1, 2, 3 \ldots, (n-1)$; *i.e.* in all n different values.

Thus, when $n = 1$, the possible value of $l = 0$

when $n = 2$, the possible values of $l = 0, 1$

when $n = 3$, the possible values of $l = 0, 1, 2$ etc.

The electrons having $l = 0$, are called s-electrons. The electrons having $l = 1$ are p-electrons, with $l = 2$ are d-electrons etc. For different orbitals, we have,

Quantum number				
Principal, n	1	2	3	4
Azimuthal, l	1*s*	2*s*, 2*p*	3*s*, 3*p*, 3*d*	4*s*, 4*p*, 4*d*, 4*f*

The third quantum number (m_l describes the orientation of the wave function with respect to a given axis. For a given value of l, there are $(2l+1)$ possible m_l values, as

$l, l-1, l-2, \ldots +2, +1, 0, -1, -2, \ldots -l$

when $l = 0$, the possible values of $m_l = 0$

when $l = 1$, the possible values of $m_l = +1, 0, -1$

when $l = 2$, the possible values of $m_l = +2, +1, 0, -1, -2$

Thus an s-electron ($l = 0$) can have only one orientation. But a p-electron would have three orientations denoted by p_x, p_y, p_z (electrons). Similarly, for the d-electrons ($l = 2$) there would be five orientations.

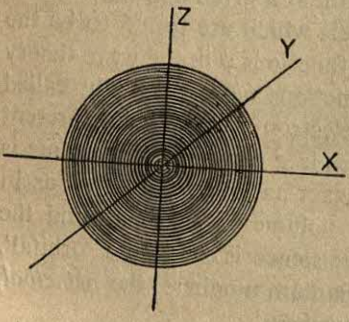


Fig. XXIV.17. 1*s* orbital

The spin quantum numbers represent the clockwise and anticlockwise rotation of the electrons. There are two possible spin quantum number ($\frac{1}{2}$ and $-\frac{1}{2}$). An orbital at most can accommodate two electrons provided they have opposite spins.

Shape of the orbitals: The probability $\psi^2 \triangle v$ depends upon the distance r from the nucleus of the small volume element ($\triangle v$) as also on the angle (θ, ϕ) it subtends to a given direction.

For an s-electron, the orbital angular momentum quantum number, $l = 0$. Hence, the wave function does not depend on θ, ϕ angles. It only depends upon the radial distance r in any direction. Hence the shape of a 1*s*, 2*s*, 3*s*, orbitals are all spherically symmetrical about the nucleus (Fig. XXIV.17).

In the case of p-electrons, the orbital angular momentum quantum number $l = 1$, and $m_l = +1, 0$ and -1. The three possible orientations (p_x, p_y, p_z) are mutually at right angles. The shapes are dependent on the angles, θ and ϕ. These are distributed as pear-shaped orbitals along x, y, and z-axes (Fig. XXIV.18).

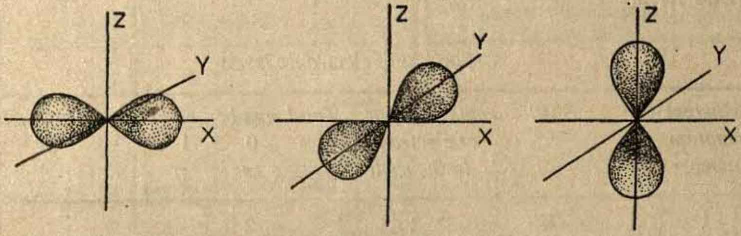


Fig. XXIV.18. p-orbitals

In the case of d-orbitals, there are five possible orientations as $l = 2$. The lobes of the orbitals may be distributed between xy, yz, zx-axes (Fig. XXIV.19). These three are denoted as d_{xy}, d_{yz}, d_{xz} orbitals. Besides these, there are two other distribution for d-orbitals called $d_{x^2-y^2}$ and d_{z^2}. In $d_{x^2-y^2}$ orbital, the two lobes lie along x and y axes, whereas in d_{z^2} orbital, the two lobes lie along z-axis with a cylindrical ring in the xy-plane.

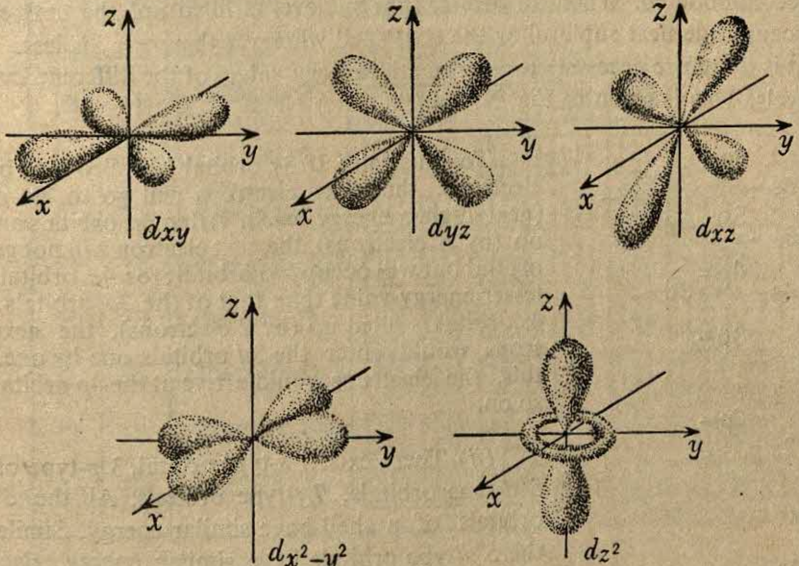


Fig. XXIV.19. d-orbitals

24-21. Electronic Configuration of atoms

The electrons present in an atom do not revolve round the nucleus haphazardly in different orbitals. There is a definite system in the accommodation of the electrons in the different orbials. It has been seen earlier that the maximum number of electrons present in the shells (*K*, *L*, *M*, *N*, *O* . . .) would be $2n^2$, where *n* is the principal quantum number of the shell. Again every shell consists of sub-levels (*s*, *p*, *d*, *f*, *g* . . .). The number of sub-levels is *n*. The number of electrons in these sublevels, *i.e.*, *s*, *p*, *d*, *f*, . . . type orbitals is given by $2(2l + 1)$. This is summarised here.

Capacities of electronic levels

Principal quantum number	*Shell*	*max. number of electrons in the shell*	*Total number of electrons in Sublevels*				
			$l =$ 0	1	2	3	4
			s	*p*	*d*	*f*	*g*
1	*K*	2	2				
2	*L*	8	2	6			
3	*M*	18	2	6	10		
4	*N*	32	2	6	10	14	
5	*O*	50	2	6	10	14	18

The arrangement of electrons in the orbitals is governed by the following rules, called 'building up' or **auf-bau** principle.

(*i*) The orbitals are filled up by electrons in the order of increasing energy (hence increasing *n*) beginning from the lowest until all the electrons of the atom are accommodated. When an orbital in a sublevel is filled up, the next electron will occupy the next sublevel or the next shell wherever the energy is less.

It is therefore necessary to ascertain the energy-values of the different levels and sublevels. This is given in Fig. XXIV.20.

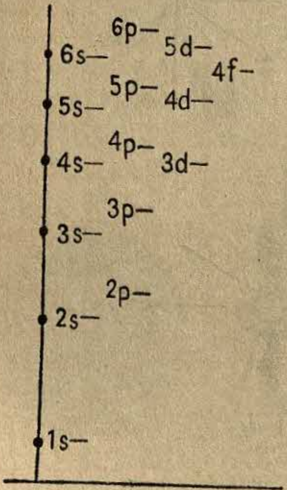


Fig. XXIV.20. Energy levels of orbitals (diagrammatic)

To illustrate: If 3*s* orbital be filled up by two electrons, the next electrons will go to 3*p* orbitals (next higher energy-level). After 3*p* orbitals are filled up (by 6 electrons), the next electron will not go to 3*d* orbital but will occupy 4*s* orbital; for 4*s* orbital has a lesser energy-value than that of the 3*d* orbitals. After 4*s* orbital is filled up (by 2 electrons), the next electrons would enter the 3*d* orbitals one by one. After this, the electrons would arrive at the 4*p* orbital. And so on.

(*ii*) There exist 1 *s*-type orbital, 3 *p*-type orbitals, 5 *d*-type orbitals, 7 *f*-type orbitals. All the 3 *p*-type orbitals of a shell have similar energy. Similarly all the 5 *d*-type orbitals have similar energy. Each one of these orbitals of any type can hold only two electrons having opposite spins.

Electrons have a tendency to maintain maximum spin. So long as vacant orbitals of similar energy are available, the entering electrons would occupy them and prefer to remain unpaired. Electrons would pair themselves only when empty orbitals of similar energy are no longer available. This is known as **Hund's Rule.**

The pictorial presentation of this rule is given in the Tables below. The spin is indicated by a single ↑ and pairing by double arrows ⇅.

TABLE A : ELECTRONIC CONFIGURATION

	At.no.	Elec. symbol	Electron distribution				
			1s	2s	2p	3s	3p
H	1	$1s^1$	[↑]				
He	2	$1s^2$	[↑↓]				
Li	3	$1s^2 2s^1$	[↑↓]	[↑]			
Be	4	$1s^2 2s^2$	[↑↓]	[↑↓]			
B	5	$1s^2 2s^2 2p^1$	[↑↓]	[↑↓]	[↑][ ][ ]		
C	6	$1s^2 2s^2 2p^2$	[↑↓]	[↑↓]	[↑][↑][ ]		
N	7	$1s^2 2s^2 2p^3$	[↑↓]	[↑↓]	[↑][↑][↑]		
O	8	$1s^2 2s^2 2p^4$	[↑↓]	[↑↓]	[↑↓][↑][↑]		
F	9	$1s^2 2s^2 2p^5$	[↑↓]	[↑↓]	[↑↓][↑↓][↑]		
Ne	10	$1s^2 2s^2 2p^6$	[↑↓]	[↑↓]	[↑↓][↑↓][↑↓]		
Na	11	$1s^2 2s^2 2p^6 3s^1$	[↑↓]	[↑↓]	[↑↓][↑↓][↑↓]	[↑]	
Mg	12	$1s^2 2s^2 2p^6 3s^2$	[↑↓]	[↑↓]	[↑↓][↑↓][↑↓]	[↑↓]	
Al	13	$1s^2 2s^2 2p^6 3s^2 3p^1$	[↑↓]	[↑↓]	[↑↓][↑↓][↑↓]	[↑↓]	[↑][ ][ ]
Si	14	$1s^2 2s^2 2p^6 3s^2 3p^2$	[↑↓]	[↑↓]	[↑↓][↑↓][↑↓]	[↑↓]	[↑][↑][ ]
P	15	$1s^2 2s^2 2p^6 3s^2 3p^3$	[↑↓]	[↑↓]	[↑↓][↑↓][↑↓]	[↑↓]	[↑][↑][↑]
S	16	$1s^2 2s^2 2p^6 3s^2 3p^4$	[↑↓]	[↑↓]	[↑↓][↑↓][↑↓]	[↑↓]	[↑↓][↑][↑]
Cl	17	$1s^2 2s^2 2p^6 3s^2 3p^5$	[↑↓]	[↑↓]	[↑↓][↑↓][↑↓]	[↑↓]	[↑↓][↑↓][↑]
Ar	18	$1s^2 2s^2 2p^6 3s^2 3p^6$	[↑↓]	[↑↓]	[↑↓][↑↓][↑↓]	[↑↓]	[↑↓][↑↓][↑↓]

TABLE B : ELECTRONIC CONFIGURATION

	At.no.	Electronic symbol	Electron distribution						
				4s	3d				
Sc	21	$1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^1$	Ar	↑↓	↑				
Ti	22	$1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^2$	Ar	↑↓	↑	↑			
V	23	$1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^3$	Ar	↑↓	↑	↑	↑		
Cr	24	$1s^2 2s^2 2p^6 3s^2 3p^6 4s^1 3d^5$	Ar	↑	↑	↑	↑	↑	↑
Mn	25	$1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^5$	Ar	↑↓	↑	↑	↑	↑	↑
Fe	26	$1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^6$	Ar	↑↓	↑↓	↑	↑	↑	↑
Co	27	$1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^7$	Ar	↑↓	↑↓	↑↓	↑	↑	↑
Ni	28	$1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^8$	Ar	↑↓	↑↓	↑↓	↑↓	↑	↑
Cu	29	$1s^2 2s^2 2p^6 3s^2 3p^6 4s^1 3d^{10}$	Ar	↑	↑↓	↑↓	↑↓	↑↓	↑↓
Zn	30	$1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^{10}$	Ar	↑↓	↑↓	↑↓	↑↓	↑↓	↑↓

Thus, of the six electrons in the *p*-orbital, the first three would occupy singly the three p_x, p_y, p_z orbitals. From the fourth electron, the pairing shall ensue. Similarly in the five *d*-orbitals pairing shall begin only when the sixth electron enters this sublevel.

In writing out the electronic arrangement in an atom, the numbers of electrons present in different sublevels (*s*, *p*, *d*, . . .) are incicated by indices at the upper right of the letter expressing the sublevel of the orbital. The shell is expressed by writing the principal quantum number (1, 2, 3, . . .) before the sublevel concerned. Thus, $3s^2 3p^4$, means there 2 electrons in the *s*-orbital and 4 electrons in the *p*-orbital of the *M*-shell (3rd quantum level). The twelve electrons of the Magnesium atom is written as

$$\text{Mg} \rightarrow 1s^2\ 2s^2\ 2p^6\ 3s^2$$

Other examples:	At. no.	Electronic configuration
Sulphur	16	$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^4$
Argon	18	$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6$
Chromium	24	$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^5\ 4s^1$
Barium	56	$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^{10}\ 4s^2\ 4p^6\ 4d^{10}\ 5s^2\ 5p^6\ 6s^2$

24-22. Electronic arrangement and the Periodic Table

In the periodic table the elements are arranged in order of the increasing atomic numbers. For each increase in atomic number, one electron has to be added. This is governed by the *auf-bau* principle. Each *period* of the table corresponds to the gradual filling up of the quantum level with all its sublevels. When the shell is completely filled up the next period begins. A brief account of this arrangement is given here.

The first element hydrogen ($Z = 1$) has only one electron. For the normal state of the atom, the electron should be in a $1s$-electronic quantum state. The next element is *He* ($Z=2$). The two electrons can both come into $1s$-orbit, whereby the potential energy will be a minimum. The arrangement would be spherically symmetrical and there would be no residual field outside the atom. The configuration of helium is then $1s^2$, the K-shell is thus completely filled up.

With the next element lithium ($Z = 3$) an electron must occupy a position in the L-shell. Again for lowest possible energy level, two electrons of lithium shall be in K-shell and one electron in the $2s$-orbit. That is, its configuration is $1s^2 2s^1$. Lithium thus should have a valency one, which is a fact. It is comparatively much easier to remove a $2s$-electron than an $1s$ electron from this atom. That is why first ionisation potential of lithium is 5.39 volts and 2nd ionisation potential is 75.6 volts

Beryllium, the next atom in the Periodic Table ($Z = 4$) has two electrons in $1s$ and two in $2s$ orbit, having the configuration $1s^2 2s^2$. It is obvious that K-shell is completed and the s-subgroup of L-shell is also filled up. With boron ($Z = 5$), the added electron will have to occupy a place in the p-orbit of the L-shell as the other lower energy-levels are already filled up. The electronic configuration for boron is then $1s^2 2s^2 2p^1$. This process of gradual filling up of shells and subshells will continue until we reach the turning point at neon ($Z = 10$), when both K-shell and L-shell are completed with electrons. Neon is then $1s^2 2s^2 2p^6$.

The eleventh atom is sodium, immediately after the inert neon. Since K- and L-shells are fully occupied by ten electrons, the eleventh electron, for the minimum of potential energy, will take a place in M-shell at s-subgroup, *i.e.*, its configuration will be $1s^2 2s^2 2p^6 3s^1$. This process will continue until we reach argon ($Z = 18$), when K-shell, L-shell and s and p-subgroups of M-shell are completed (see the table). It will be noticed that after the completion of each shell, a new period begins as is expected from chemical data. The completion of a shell or subshell means the most stable positions with weak external field and hence chemical inertness. The valency is really determined by the extent of incompleteness of the outermost shell.

The configuration of argon is $1s^2 2s^2 2p^6 3s^2 3p^6$. In the next element potassium ($Z = 19$) we expect that the 19th electron (beyond the argon configuration) should take a position in $3d$-state (*i.e.*, $n = 3$, $l = 2$). But potassium closely resembles lithium and sodium in its chemical characters and further, these produce identical spectra. These spectra are caused by the electrons at the periphery. It is therefore suggested that the 19th electron will occupy a place in the $4s$-state than in $3d$-state. Theoretical calculation later indicated that the potental energy in

4*s*-state in the atom is less than that in the 3*d*-state. The electronic structure of potassium should then be $1s^2 2s^2 2p^6 3s^2 3p^6 4s$.

In Calcium (Z = 20) 3*d*-sublevel is not occupied but two electrons go to 4*s*-level; Ca, $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2$. After calcium, however, 3*d*-sublevel begins to be gradually completed until we come to Zinc (Z = 30). Beyond zinc, since 4*s*-subgroup is already filled up, electrons successively add themselves to 4*p*-subgroup. On the completion of 4*p*-subgroup, we arrive at (Z = 36) Krypton, having the configuration, $1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^6$.

The table however indicates that the 3*d*-sublevel is already completed with Copper (Z = 29), the configuration shown is $1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^1$. This means that copper should behave like an alkali metal with one electron in 4*s*-orbital. But this is not so, the 3*d*-levels and 4*s*-levels are so close in copper that bivalent Cu^{++} ions are readily formed.

The sequence of metals from Sc (Z = 21) to Cu (Z = 29) form the transitional elements. In these also 3*d*- and 4*s*-levels are quite close and that is why they are apt to show variable valence and coloured compounds.

The element following Kr is Rubidium (Z = 37), which is a typical alkali metal and has a 5*s*-electron in spite of 4*d*- and 4*f*-levels remaining unfilled. Similarly, in the following element Sr we have two 5*s*-electrons and it behaves like calcium. From the next element Y(Z = 39) the 4*d*-levels are lower than 5*p*, so commencing from element Y(Z = 39) to element Ag (Z = 47) the 4*d*-levels are first filled up. These elements constitute the second transitional series.

Silver (Z = 47) has a configuration like that of copper and next element Cd like that of mercury. These two elements have 4*d*-levels completed and have 1 and 2 electrons in 5*s*-level.

The 5*s*- and 5*p*-orbitals are completed with xenon which is followed by the alkali metal Cs with one 6*s*-electron and Ba with two 6*s*-electrons.

In the next element lanthanum, the added electron enters the 5*d*-level and a next transitional series is expected as with scandium earlier. But with the rise in atomic numbers (Z) it was found that 4*f*-levels are now sufficiently low and this level is first filled up in preference to 5*d*-level. The maximum number of electrons that can be accommodated in 4*f*-level ($l = 3$) is $2(2l + 1)$, *i.e.*, $2(2 \cdot 3 + 1) = 14$. So 14 elements from Ce to Lu are obtained in which successively the 4*f*-levels are filled up. All these fourteen elements have outer configuration $5s^2 5p^6 6s^2$. This is why these 14 rare earth elements, as they are called, have identical chemical properties and their separation is so difficult.

Hafnium comes after the rare earth elements with (Z = 72), with the outer configuration $5d^2 6s^2$. After hafnium, 5*d*-orbital is filled up producing another transitional series. Then begins the building up of the 6*p*-levels. This ends with radon with an outer $6s^2 6p^6$ structure and hence inert in character. The same procedure continues after radon with the radioactive transuranic elements. Careful observation of the table would indicate that with Ac, 5*f*-shell begins to be filled instead of 6*f*- or 7*p*-levels. The result is, like lanthanide rare earths, a series of similarly behaving elements begin from Ac(Z = 89) and are called Actinide rare earth elements.

THE ARRANGEMENT OF ELECTRONS IN THE ATOMS OF THE ELEMENTS IN THEIR GROUND STATES

		1*s*	2*s*	2*p*	3*s*	3*p*	3*d*	4*s*	4*p*	4*d*	4*f*	5*s*	5*p*	5*d*	5*f*	6*s*	6*p*	6*d*	7*s*	
	1 H	1																		
	2 He	2																		1*s* Full
	3 Li	2	1																	
	4 Be	2	2																	2*s* Full
	5 B	2	2	1																
	6 C	2	2	2																
	7 N	2	2	3																
	8 O	2	2	4																
	9 F	2	2	5																
	10 Ne	2	2	6																2*p* Full
	11 Na	2	8		1															
	12 Mg	2	8		2															3*s* Full
	13 Al	2	8		2	1														
	14 Si	2	8		2	2														
	15 P	2	8		2	3														
	16 S	2	8		2	4														
	17 Cl	2	8		2	5														
	18 A	2	8		2	6														3*p* Full
	19 K	2	8		8			1												
Transition elements	20 Ca	2	8		8			2												4*s* Full
	21 Sc	2	8		8		1	2												
	22 Ti	2	8		8		2	2												
	23 V	2	8		8		3	2												
	24 Cr	2	8		8		5	1												
	25 Mn	2	8		8		5	2												
	26 Fe	2	8		8		6	2												
	27 Co	2	8		8		7	2												
	28 Ni	2	8		8		8	2												
	29 Cu	2	8		8		10	1												
	30 Zn	2	8		8		10	2												3*d* Full
	31 Ga	2	8			18		2	1											
	32 Ge	2	8			18		2	2											
	33 As	2	8			18		2	3											
	34 Se	2	8			18		2	4											
	35 Br	2	8			18		2	5											
	36 Kr	2	8			18		2	6											4*p* Full
	37 Rb	2	8			18		8				1								
	38 Sr	2	8			18		8				2								5*s* Full
Transition elements	39 Y	2	8			18		8		1		2								
	40 Zr	2	8			18		8		2		2								
	41 Nb	2	8			18		8		4		1								
	42 Mo	2	8			18		8		5		1								
	43 Tc	2	8			18		8		6		1								
	44 Ru	2	8			18		8		7		1								
	45 Rh	2	8			18		8		8		1								
	46 Pd	2	8			18		8		10										
	47 Ag	2	8			18		8		10		1								
	48 Cd	2	8			18		8		10		2								4*d* Full
	49 In	2	8			18			18			2	1							
	50 Sn	2	8			18			18			2	2							

THE ARRANGEMENT OF ELECTRONS IN THE ATOMS OF THE ELEMENTS IN THEIR GROUND STATES

		1*s*	2*s*	2*p*	3*s*	3*p*	3*d*	4*s*	4*p*	4*d*	4*f*	5*s*	5*p*	5*d*	5*f*	6*s*	6*p*	6*d*	7*s*	
	51 Sb	2		8		18			18			2	3							
	52 Te	2		8		18			18			2	4							
	53 I	2		8		18			18			2	5							
	54 Xe	2		8		18			18			2	6							5*p* Full
Transition elements	55 Cs	2		8		18			18				8			1				
	56 Ba	2		8		18			18				8			2				6*s* Full
Rare earths or lanthanons	57 La	2		8		18			18				8	1		2				
	58 Ce	2		8		18			18		2		8			2				
	59 Pr	2		8		18			18		3		8			2				
	60 Nd	2		8		18			18		4		8			2				
	61 Pm	2		8		18			18		5		8			2				
	62 Sm	2		8		18			18		6		8			2				
	63 Eu	2		8		18			18		7		8			2				
	64 Gd	2		8		18			18		7		8	1		2				
	65 Tb	2		8		18			18		9		8			2				
	66 Dy	2		8		18			18		10		8			2				
	67 Ho	2		8		18			18		11		8			2				
	68 Br	2		8		18			18		12		8			2				
	69 Tm	2		8		18			18		13		8			2				
	70 Yb	2		8		18			18		14		8			2				
	71 Lu	2		8		18			18		14		8	1		2				4*f* Full
	72 Hf	2		8		18			32				8	2		2				
	73 Ta	2		8		18			32				8	3		2				
	74 W	2		8		18			32				8	4		2				
	75 Re	2		8		18			32				8	5		2				
	76 Os	2		8		18			32				8	6		2				
	77 Ir	2		8		18			32				8	7		2				
	78 Pt	2		8		18			32				8	9		1				
	79 Au	2		8		18			32				8	10		1				
	80 Hg	2		8		18			32				8	10		2				5*d* Full
	81 Tl	2		8		18			32				18			2	1			
	82 Pb	2		8		18			32				18			2	2			
	83 Bi	2		8		18			32				18			2	3			
	84 Po	2		8		18			32				18			2	4			
	85 At	2		8		18			32				18			2	5			
	86 Rn	2		8		18			32				18			2	6			6*p* Full
	87 Fr	2		8		18			32				18			8			1	
	88 Ra	2		8		18			32				18			8			2	7*s* Full
Actinons	89 Ac	2		8		18			32				18			8		1	2	
	90 Th	2		8		18			32				18			8		2	2	
	91 Pa	2		8		18			32				18		2	8		1	2	
	92 U	2		8		18			32				18		3	8		1	2	
	93 Np	2		8		18			32				18		5	8			2	
	94 Pu	2		8		18			32				18		6	8			2	
	95 Am	2		8		18			32				18		7	8			2	
	96 Cm	2		8		18			32				18		7	8		1	2	
	97 Bk	2		8		18			32				18		9	8			2	
	98 Cf	2		8		18			32				18		10	8			2	
	99 En	2		8		18			32				18		11	8			2	
	100 Fm	2		8		18			32				18		12	8			2	
	101 Md	2		8		18			32				18		13	8			2	
	102 No	2		8		18			32				18		14	8			2	

Thus we see how a beautifully simple scheme explains the entire classification of the elements indicating the regular variation in their properties. We have thus gained an insight into the structure of the atoms.

A glance at the tables above for electronic arrangement shows that the outermost shell of an atom never has more than eight electrons and the outer penultimate shell has a maximum of eighteen electrons. All the inert gases have eight electrons in the outermost shell having s^2p^6 distribution completely filling the *s*- and *p*-orbitals. And the inert gases are chemically most inactive. On the other hand, the elements which closely precede or follow the inert gases in the Table are found to be strongly chemically reactive. Those which precede, *e.g.*, F, O. S, Cl, Br, etc., are electronegative and those which follow, *e.g.*, Na, Mg, K, Ca, etc., are electropositive. Because of the contrasting electrical character, the atoms of elements preceding an inert gas readily combines with those of elements following an inert gas, *e.g.*, sodium spontaneously unites with chlorine. The valence of the elements is determined by the distance of the position of the element from the inert gas, *e.g.*, 1 for sodium and for chlorine, 2 for oxygen and magnesium, 3 for aluminium and phosphorus, etc. The recurrence of the common characteristics in the different columns justifies the statement that properties of the elements are periodic functions of their atomic numbers.

The chemical activity of an atom depends upon the magnitude of its external electric field. The atoms of the inert gas elements not only show lack of chemical activity but also exhibit little tendency to form polyatomic molecules or to condense easily into liquids or solids. All the inert gases are monatomic and have very low boiling points. It may then be reasonably concluded that electronic arrangement in the inert gas atoms is such that these have very weak fields at the periphery. In other words, the arrangement of electrons in the atoms of inert gases must be such as to have especially low energy, *i.e.*, the most stable arrangement. The atom of an element which follows an inert gas in the Table has one or two electrons outside the stable inert gas core. These electrons are easily detachable yielding positive ions, *e.g.*, K-atom will lose an electron to form the stable argon core with a unit + *ve* charge. In fact, in the solid state these easily detachable electrons become somewhat loose as to render these elements good conductors of electricity.

On the other hand, the elements preceding inert gases, require one or two electrons to attain the inert gas core. That is why elements, like chlorine, preceding inert gases easily pick up electrons to produce negative ions. Since these elements have no extra electrons to spare to become loose, these are non-conductors. This scheme thus naturally explains the metallic and non-metallic characters of the elements.

EXERCISES

1. Name the fundamental constituents of an atom and mention their characteristics. Explain how these particles build up the atom. How is the number of these particles in an atom related to the atomic number and atomic weight?

Write down the electronic structures of elements having atomic no. 29 and 36.

2. (*a*) How was it established that 'electrons are an essential constituent of all atoms'?
   (*b*) Discuss the principles involved in the determination of the charge of an electron by two methods.

3. (*a*) Explain why is it assumed that every atom has a positively charged nucleus which occupies a small volume. (*Burdwan B.Sc.*) (*b*) What is the experimental evidence that an atom is mostly an open space? (*Gorakhpur B.Sc.*) (c) Give an account of the experiments which led to the discovery of the nucleus. (*Madras B.Sc.*)

4. Write a note on Moseley's work on the X-ray spectra of elements. (*Burdwan B.Sc., Madras B.Sc.*)

5. Narrate the Rutherford's concept of atomic model. What were the drawbacks of Rutherford's model?

6. Enunciate Bohr's postulates. How does Bohr's theory explain structure of atomic spectra of hydrogen (*Burdwan B.Sc., Allahabad B.Sc., Mysore B.Sc.*).

7. Write a critical discussion on 'Bohr Theory of Hydrogen Atom.' (*Calcutta B.Sc. Hons.*)

8. State Bohr's criterion for stationary orbits in an atom. Calculate the frequency of light radiated when an electron in an excited state falls from the second orbit to the first orbit. (Use standard values for e, h and m). (*Allahabad B.Sc.*)

9. Calculate the wavelength of the 1st line of the Balmer series. (Rydberg constant = 109700 cm^{-1}). (*Madras B.Sc.*) **[Ans.** 7563 Å]

10. What modifications were proposed by Somerfeld for the Bohr's theory and why?

11. (*a*) Write explanatory notes on : (*i*) stability of the nucleus (*ii*) quantum numbers.
    (*b*) What are meant by (*i*) Rydberg constant (*ii*) Planck constant? Give their values.

12. Show that the Bohr's radius for the third orbit of H-atom is 477 pm.

13. (*a*) Derive de Broglie's equation regarding wave particle duality and explain its significance.

(b) Mention an experimental evidence to show that an electron has a wave nature. What is the difference between a radiation wave and a de Broglie wave?

(c) What is the wavelength associated with a particle of mass 0.1 mg moving with a speed of 1×10^5 cm/sec? **[Ans.** $6.62 \times {}^{10-28}$ cm]

14. State Heisenberg's Uncertainty Principle. Show that it is valid only for small particles and not for large objects. (*Madras B.Sc.*)

15. What is an orbital? In what ways does it differ from a Bohr orbit? Sketch the three p-type orbitals explaining their directional character.

16. What are quantum numbers? What is Pauli's exclusion principle? What is Hund's rule? Illustrate with examples. Write the electronic configurations of ^{16}O, ^{12}C, ^{14}N, ^{32}S, and ^{29}Cu. (*Madras B.Sc.*).

17. Explain with illustrations:

(*a*) l-value determines the shape of an orbital

(*b*) there cannot be more than 5 d-type orbitals

(*c*) p-orbital cannot contain more than six electrons

(*d*) each of the three p-orbitals of the N-atom has an unpaired electron.

18. Show how auf-bau principle helps in the building up of the electronic arrangement in atoms of elements.

19. (*a*) What do the following configurations represent?

(*i*) $1s^2\,2s^2\,2p^6\,3s^2\,3p^6\,4s^2$

(*ii*) $1s^2\,2s^2\,2p^6\,3s^2\,3p^6\,3d^9$

(*iii*) $1s^2\,2s^2\,2p^6\,3s^2\,3p^6\,3d^{10}\,4s^2\,4p^5$

(*b*) Give the values of all the four quantum numbers of the eight electrons of the oxygen atom. (*Allahabad, B.Sc.*)

20. Explain briefly the physical significance of ψ and ψ^2 in Schrödinger equation.

21. Estimate approximately the density of the bare nucleus of a sodium atom.

22. Express the following electrons in quantum notation having quantum numbers:

(*i*) $n = 2, \quad l = 1 \quad m_l = -1$

(*ii*) $n = 3 \quad l = 1 \quad m_l = +1$

23. Which involves higher energy, β-emission or a detatchment of an electron from the outermost orbit and by how much approximately?

24. Express in quantum orbital notation (nl^x) the configurations of elements having atomic numbers 7, 17 and 20.

25. Which of the following configurations would you accept for the ground state of beryllium atoms and why?

(*i*) $1s^2\,2s^2$ (*ii*) $1s^2\,2s^1\,2p^1$.

CHAPTER 25

RADIOACTIVITY

In Sec. 24.6, radioactivity has only been defined and the properties of radioactive radiations have been mentioned. A somewhat more detailed discussion about this phenomenon may now be made.

25-1. Natural Radioactivity

The elements having atomic weights greater than that of lead are all radioactive. The nuclei of these elements spontaneously disintegrate with emission of radiations. The rays emitted may be of three types, α, β or γ-rays.

In 1903, Rutherford and Soddy proposed that the nuclei of very heavy elements (having atomic numbers greater than 82) are unstable and these decompose spontaneously emitting an α or a β particle. This leads to the formation of a new element with different physical or chemical properties. The product of radioactive disintegration may itself be radioactive and undergo further disintegration. Thus a genetic series of radioactive elements occur; the process continues until a stable nucleus of lead or one of its isotopes is formed.

The first radioactive element discovered is uranium. It is an element of the 6th group of the periodic table with the atomic number 92 and atomic mass 238. It emits spontaneously an α-particle to be transformed into Uranium-X_1 (*i.e.*, UX_1). The daughter UX_1 will have an atomic mass 4 units less and charge 2 units less than those of uranium (*i.e.*, at. wt. = 234, at. no. = 90). UX_1 is also radioactive and emits a β-particle to produce UX_2. Due to loss of a β-particle the nuclear charge will increase by unity, the mass remaining the same. UX_2 in its turn is transformed into U_{II} by ejecting a β-particle and so the process continues until finally the non-radioactive lead is formed. At each stage either an α- or a β-particle is emitted. When an α-particle goes out, the mass decreases by 4 and charge by 2 units; when a β-particle is ejected the mass remains unaltered but charge increases by unity.

$$^{238}U_I \xrightarrow{\alpha} {}^{234}UX_1 \xrightarrow{\beta} {}^{234}UX_2 \xrightarrow{\beta} {}^{234}U_{II} \xrightarrow{\alpha} {}^{230}Io \xrightarrow{\alpha} {}^{226}Ra \longrightarrow \text{etc.}$$

This chain of consecutive radioactive transformation from uranium to lead, commonly called the Radioactive series of Uranium, is described below indicating also the variations in mass and charge (*i.e.*, atomic number) of the nucleus. Radium is but a product in this chain being derived from Ionium (Io) and being disintegrated to Radon (Rn).

TABLE : RADIOACTIVE SERIES OF URANIUM

Name and Symbol	*Particle emitted*	*Atomic mass*	*Atomic number*	*Half life*
Uranium I, (U)	α	238	92	4.6×10^{9} years
Uranium X_1, (UX_1)	β	234	90	24.1 days
Uranium X_2, (UX_2)	β	234	91	1.14 min.
Uranium II, (U_{II})	α	234	92	2.7×10^{5} years
Ionium, (Io)	α	230	90	8.3×10^{4} years
Radium, (Ra)	α	226	88	1590 years
Radon, (Rn)	α	222	86	3.8 days
Radium A, (RaA)	α	218	84	3.0 min.
Radium B, (RaB)	β	214	82	26.8 min.
Radium C, (RaC)	β, α	214	83	19.7 min.
$\beta\swarrow\ \searrow\alpha$ Radium C′ Radium C″ $\alpha\searrow\ \swarrow\beta$	α, β	214, 210	84, 81	10^{-4} sec/1.3 min.
Radium D, (RaD)	β	210	82	22 years
Radium E, (RaE)	β	210	83	5 days
Radium F, (RaF)	α	210	84	140 days
Radium G, (RaG) (Pb)	×	206	82	Stable

Two other radioactive series met with in nature start with Thorium and Protoactinium. These series are also given here.

TABLE : RADIOACTIVE SERIES OF THORIUM

Name and Symbol	*Particle emitted*	*Atomic mass*	*Atomic number*	*Half life*
Thorium, (Th)	α	232	90	1.4×10^{10} years
Mesothorium, ($MsTh_I$)	β	228	88	6.7 years
Mesothorium, ($MsTh_{II}$)	β	228	89	6.13 hours
Radiothorium, (RaTh)	α	228	90	1.9 years
Thorium X, (ThX)	α	224	88	3.65 days
Thoron (Tn)	α	220	86	55 sec.
Thorium A, (ThA)	α	216	84	0.16 sec.
Thorium B, (ThB)	β	212	82	10.6 hours
Thorium C, (ThC)	β, α	212	83	1 hour
$\beta\swarrow\ \searrow\alpha$ Thorium C′, Thorium C″ $\alpha\searrow\ \swarrow\beta$	α, β	212, 208	84,81	3×10^{-7} sec./3 min.
(Thorium D) Lead, (Pb)	×	208	82	Stable

TABLE : RADIOCATIVE SERIES OF ACTINIUM

Name and Symbol	*Particle emitted*	*Atomic mass*	*Atomic number*	*Half life*
Protoactinium, (Pa)	α	231	91	3.2×10^4 years
Actinium, (Ac)	β	227	89	13.5 years
Radioactinium, (RaAc)	α	227	90	19 days
Actinium X, (AcX)	α	223	88	11.2 days
Actinon (An)	α	219	86	3.9 sec.
Actinium A, (AcA)	α	215	84	1.8×10^{-3} sec.
Actinium B, (AcB)	β	211	82	36 min.
Actinium C, (AcC)	β, α	211	83	2.16 min.
$\beta \swarrow \searrow \alpha$ Actinium C′, Actinium C″	α, β	(211, 207)	84, 81	5×10^{-3} sec./4.7 min.
$\alpha \searrow \swarrow \beta$ Actinium D (Lead) (Pb)	×	207	82	Stable

25.2. Law of Radioactive Disintegration

The radioactivity of an element is independent of temperature and physical condition and environment. It is also unaffected by chemical combination with other elements. The energy associated with radioactive disintegration is of the order of 10^9 calories per mole whereas in a chemical reaction it is of the order of 10^5 calories per mole.

The rate of disintegration of an element at any instant of time is proportional to the number of atoms (n) *present*; *i.e.*,

$$-dn/dt = \lambda n \qquad \ldots \text{(XXV.1)}$$

where λ is called the disintegration constant and is characteristic of the given element. Integrating this equation,

$$\lambda = \frac{1}{t} \ln \frac{n_0}{n}, \qquad \text{where } n_0 = \text{initial number of atoms}$$

or

$$n/n_0 = e^{-\lambda t} \qquad \ldots \text{(XXV.1a)}$$

It is a first order reaction, hence the half-life of a radio-element (Sec. 17.4) would be,

$$t_{\frac{1}{2}} = \ln 2/\lambda = 0.693/\lambda \text{ (constant)} \qquad \ldots \text{(XXV.2)}$$

The time required for 50% decomposition is thus independent of the initial amount and is specific for a given element. The half-life may be as high as 10^9 years or it may be as small as 10^{-6} sec.

'The half-life period of Ra is 1600 years' means that of any given quantity of radium one half would disintegrate in 1600 years. Again after another 1600 years, one half of the remaining 50% radium would disintegrate. That is, in 3200 years (50% + $\frac{1}{2}$ of 50%) or 75% of the original amount of radium would decay.

Since the decay law is an exponential one, complete disintegration theoretically would require infinite time. The is illustrated in Fig. XXV.1.

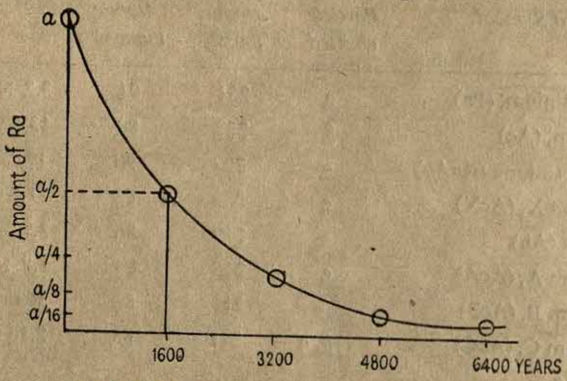


Fig. XXV.1. Disintegration rate of Radium

25.3. Radioactive Equilibrium

Suppose a radioactive element (A) disintigrates to produce the daughter element (B), which is also radioactive. Suppose also λ_A and λ_B are the rate constants of disintegration of A and B. The rate of decay of each of these will be governed by eqn. XXV.1. If n_A be the number of atoms of A at any time, then the rate at which B is produced is $n_A\lambda_A$. The rate at which B disintegrates is $n_B\lambda_B$, where n_B is the number of B atoms present. When the 'steady state', commonly called *radioactive equilibrium*, is attained, the rate of formation of B and its disintegration rate would be the same; *i.e.*,

$$n_A\lambda_A = n_B\lambda_B.$$

Hence

$$n_A/n_B = \lambda_B/\lambda_A = t_{\frac{1}{2}(A)}/t_{\frac{1}{2}(B)} \qquad \ldots(\text{XXV.3})$$

Allowing sufficient time, the equilibria in a radioactive series is given by,

$$n_A\lambda_A = n_B\lambda_B = n_C\lambda_C = n_D\lambda_D = \ldots$$

The radioactivity of an element is expressed in units of '*curie*' (*c*). A curie is defined as the quantity of the radioactive material in which 3.70×10^{10} disintegrations occur per second. The smaller unit is the '*microcurie*' (μc) having 3.70×10^4 disintegrations per second. The number of atoms present in 1 curie is then $(3.7 \times 10^{10})/\lambda$.

25.4. Average Life

In a small time interval dt, the number of atoms which disintegrate is dN. If starting from a given instant, the time t is recorded, then dN represents the number of atoms having life-span t. The total number of atoms N_0 is composed of such small numbers, dN_1, dN_2, dN_3, etc. with life-spans t_1, t_2, t_3, etc. Hence the average-life of the radio-element would be.

$$t_{av} = \frac{t_1dN_1+t_2dN_2+t_3dN_3+\ldots}{N_0} = \int_0^\infty \frac{tdN}{N_0} = \int_0^\infty \frac{t\lambda Ndt}{N_0}, \text{ (from eqn. XXV.1)}$$

$$= \int_0^\infty t\lambda.e^{-\lambda t}dt = \frac{1}{\lambda} \qquad \ldots(\text{XXV.4})$$

Now, $$t_{av} = \frac{1}{\lambda} \text{ and } t_{\frac{1}{2}} = \frac{ln\,2}{\lambda} = \frac{0.693}{\lambda}$$

$$\therefore \quad t_{av} = t_{\frac{1}{2}} \times \frac{1}{0.693} = 1.44 \times t_{\frac{1}{2}} \qquad \text{. . . (XXV.4a)}$$

Example 1. The half-life of ^{232}Th is 1.4×10^{10} years and that of its daughter element ^{228}Ra is 7 years. What is the weight of ^{228}Ra in equilibrium with 1 gm of ^{232}Th?

Let w be the wt. of ^{228}Ra in equilibrium.

We know $$\frac{n_{\text{Th}}}{n_{\text{Ra}}} = \frac{t_{\frac{1}{2}(\text{Th})}}{t_{\frac{1}{2}(\text{Ra})}}$$

$$\therefore \quad \frac{N_0/232}{wN_0/228} = \frac{1.4 \times 10^{10}}{7} = 2 \times 10^9 \quad (N_0\text{, Avogadro number})$$

or $$w = 228/(232 \times 2 \times 10^9) = 5 \times 10^{-10} \text{ gm}$$

Example 2. $^{238}_{92}$U disintegrates ultimately into $^{206}_{82}$Pb. How many α- and β-particles are emitted per uranium atom in this change?

Loss of weight $= 238-206 = 32$

Hence, no. of α-particles emitted $= 32 \div 4 = 8$

Loss of nuclear charge $= 92-82 = 10$

For the loss of 8 α-particles, charge loss $2 \times 8 = 16$ units. If x β-particles are emitted, the gain in charge $= 1 \times x$

Hence $16-x = 10$, or $x = 6$

That is, 8α- and 6 β-particles are emitted.

Example 3. Two gm of a radioactive substance decayed to 0.5 gm in 60 hours. In what time will it be reduced to 10% of its initial amount?

Initial amount $a = 2$ gm, $a-x = 0.5$ gm.

$$\therefore \quad \lambda = \frac{1}{t} \ln \frac{a}{a-x} = \frac{2.303}{60} \log \frac{2}{0.5} = 2.32 \times 10^{-2} \text{ hr}^{-1}$$

Now the required time (t) for decay to 10%,

$$t = \frac{1}{\lambda} \ln \frac{a}{a-x} = \frac{2.303}{2.32 \times 10^{-2}} \log \frac{2}{0.2} = 99.2 \text{ hr}$$

25.5. Group Displacement Law

With the emission of an α-particle, the nucleus of the atom loses two units of positive charge and hence the atomic number is reduced by two. So, the daughter element will be displaced two places to the left of the parent element in the Periodic Table. On the other hand, an emission of a β-particle increases the positive charge of the nucleus by unity and so the atomic number increases by unity. Hence the daughter element will be one place to the right of the parent element. Fazan, Russel and Soddy (1913) summarised this in the form of a law called *Group Displacement Law* which states:

"*When an α-particle is emitted in a radioactive change the product is displaced two places or groups to the left in the Periodic Table, the emission of a negative β-particle results in the displacement of one place to the right.* The law is universally followed in all the radioactive series. The displacements in the Periodic Table for the Uranium series is shown in the Fig. XXV.1a.

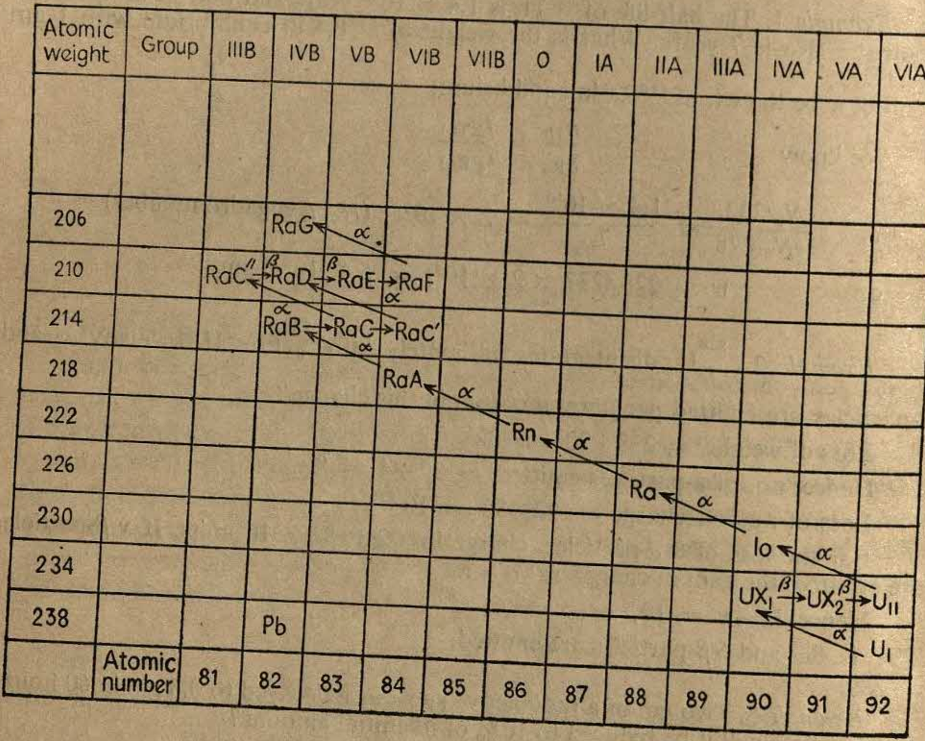


Fig. XXV.1a. Group displacement law

25.6. Isotopes

A glance at the radioactive series will reveal that there are radioactive elements, genetically connected, which have the same atomic number but with different atomic masses. Since the atomic number is the same, there shall be identity of properties. U_I and U_{II} will bear this out. Both have atomic number 92, but their atomic weights are 238 and 234, and these two have different radioactivity. Many other such examples may be easily found. Now, the atomic number is the ordinal number of the position of an element in the periodic table. Both U_I and U_{II} therefore should be given the same place in the periodic table. Their identical properties also demand the same. Such groups of elements which differ in atomic masses but have the same atomic number have been given the name '*isotopes*' by Soddy.

Experimental evidence indicating the existence of isotopic elements had already accummulated even before such a possibility could be realised from the study of radioactive series. A very careful estimation of the atomic weight of lead obtained from different sources showed a considerable variation. Lead obtained from thorite was found to have an atomic weight of 207.69 while that from uranium containing ore it was 206.08. This is also the expectation from the disintegration of the radioactive series cited above. Atomic weight of lead from non-radioactive source is 207.2.

When Ionium, parent of Radium, was discovered by Boltwood (1906), he found that its properties were identical with those of thorium. When their salts were mixed, attempts to separate them failed. Moreover, the spectra of the two elements were identical (*i.e.*, atomic number is same). And yet their atomic masses were different. Many other instances of complete identity of properties and their inseparability were noticed, *e.g.*, Radium-D, Thorium-D and Lead; Uranium-I and Uranium-II; Radioactinium and Thorium, Radium and Mesothorium-I, etc. The three gaseous emanations had also been found to have identical properties analogous to inert gases.

It is easily understood that in isotopic elements the number of protons must be the same as the atomic number is the same. Since the atomic mass is different, the number of the constituent neutrons must vary. Thus, in the different varieties of lead, the number of protons is always 82 but number of neutrons are 122, 124, 125, and 126. In other words, the association of different number of neutrons with a definite number of protons gives rise to isotopes.

Though the isotopes were first detected with radioactive elements, most other non-radioactive elements have been shown to have isotopes. Attempt to confirm different mass in the atoms of the same element experimentally began with the investigations of Thomson and met with extra-ordinary success.

25.7. Mass Spectrograph

The positive rays or canal rays coming out through the holes of the cathode in a cathode-ray tube consist of positively charged particles. Thomson made a careful study of these rays. When an electric and a magnetic field were simultaneously applied, the particles were deflected from their original path. The displacements were recorded in a photographic plate. It was found that all particles were not affected equally and different distinct and sharp photographic images were produced. These images indicated particles of different e/m values. Since e is the same, there must be particles of different masses. The 'positive ray analysis' of Thomson showed that Neon atoms (at. wt. 20.18) are really of two types corresponding to masses of 20 and 22. Soon after more convincing evidence came from Aston's experiments.

Aston's Mass Spectrograph. Considerable improvement on Thomson's method was made by Aston (1919) with an arrangement since named Aston's Mass Spectrograph. A narrow beam of positive rays emerging out of a pierced cathode was rendered into an extremely fine ribbon by passing through co-axial slits (s_1 and s_2) of approximately 0.02 mm diameter. This fine beam then entered into an electric field maintained by two capacitor plates P_1 and P_2 and was deflected (Fig. XXV.2). The different particles, even with same mass, were deflected differently as the velocities differed, *i.e.*, the beam spread out. A portion of this spread out rays then passed through a small opening of a diaphragm D and were subjected to a magnetic field H in such a way that the particles were deflected in the same plane but in an opposite direction. The result was that the spread out rays would tend to converage. In fact, by proper adjustment of the apparatus and careful manipulation of the applied fields, it was possible to converge the rays (having particles of the same mass) at a point P on a photographic plate, where a sharp line was obtained. For particles with a different mass, a separate line would be formed. In fact, there would be distinct lines on the photographic plate for each kind of particles, like the lines of an optical spectra. Hence, this was termed mass spectrograph. In fact, different lines were formed on the plate P. The mass of the particle corresponding to a line was evaluated by comparing with a line produced by particles of known mass, say $O^+ = 16$, or $C^+ = 12$.

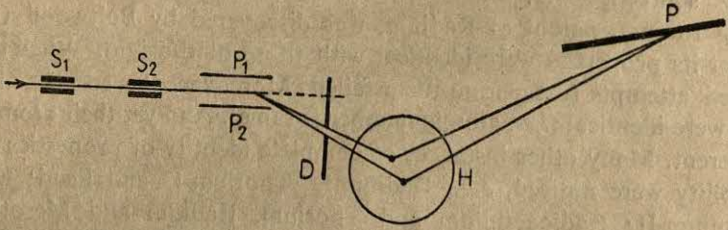


Fig. XXV.2. Principle of Aston's Mass spectrograph

With the mass spectrograph, it was not only possible to detect the isotopes of an element and their relative abundance in a sample, but also the masses of the isotopes with an accuracy of one in ten thousand*. Later more refined and different mass-measuring techniques developed in the hands of Dempster, Bainbridge, Neir, etc. We may describe here the Bainbridge technique.

Bainbridge's Mass Spectrograph. His technique is based on the fact that if a beam of ions all having the same velocity be subjected to a magnetic field, the particles would deflect and separate into groups having the same e/m values. A fine pencil of positive rays emerging out of two narrow slits (s_1 and s_2) is led into a velocity-selector S, wich consists of two parallel plates P_1, P_2 between which an electric and a magnetic field are applied. The fields are so adjusted that the deflections take place in opposite direction. Only those particles which are undeviated by the fields would come out of the exit L of the velocity selector (Fig. XXV.3). These are the particles which are affected equally but in opposite directions. The velocity (v) of all these emerging particles is given by $v = X/H$ where X is the electric and H is the magnetic field. (see Sec. 24.2). These particles then enter into a

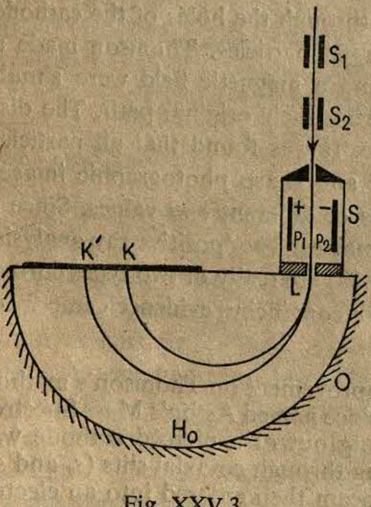


Fig. XXV.3
Bainbridges' mass spectrograph

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*For an approximate calculation, see Tolansky: Introduction to atomic physics, chapter IV. Ref: Aston: Mass spectra and isotopes, 1942.

uniform powerful magnetic field O (15000 gauss), so that these are deflected fully into a semicircle. The radius of this curvature is given by $r = \frac{mv}{eH_0}$, where H_0 is the magnetic field. Since v, H_0 and e (assuming equal charge) are constant, the radius will be directly proportional to m, mass of the particle. That is, the particles of different m will be deflected through different semicircles. Each group of particles of a definite mass strikes the plane KK′ through L and focus at a point forming a line on a photographic plate placed there. The distances LK, LK′ are thus measures of the mass of the particles of different groups. The series of lines indicate the existence of isotopes and their masses can be accurately evaluated also.

Instead of a photographic plate, if different receptacles be placed at K and K′, the isotopes would accummulate separately. It would thus be a electromagnetic method of separation of the isotopes.

With the help of these methods, it has now been possible to establish definitely that most of the elements have a number of stable isotopes. Only a few such as Be, Al, Au, Bi, etc. have no isotopes. In the table (p.494) are listed the non-radioactive elements with their isotopes.

About these isotopes, a few qualitative findings can be made. (*i*) Elements with even atomic numbers are more stable and more abundant and richer in isotopes than those containing odd number of protons. Elements with even number of neutrons are more stable and have more isotopes.

(*ii*) Stable nuclei with even mass numbers have an even number of neutrons.

(*iii*) Elements with even atomic numbers may have a number of stable isotopes, of which only one or two isotopes would have odd mass number.

The numbers of stable isotopes for different types of nuclei are as follows:

Number of protons	*Number of neutrons*	*Number of stable isotopes*
even	even	164
even	odd	55
odd	even	50
odd	odd	4

25.8. Separation of Isotopes

There are a number of methods for separation of isotopes; some of these are mentioned. We have already seen that isotopes can be separated by electromagnetic method in Bainbridge mass spectograph.

(*a*) *Diffusion method*: Through a porous barrier a gas diffuses at a rate which is inversely proportional to the square root of its mol. wt. The mixture of isotopes (or their compounds) in the gaseous form are allowed to diffuse through a clay-pipe tube when the diffuse gas is enriched in the lighter isotope. Aston, we have mentioned earlier, made the first attempt to separate Neon isotopes by this process and succeeded in concentrating ^{22}Ne to some extent. Neon normally contains 90% ^{20}Ne and 10% ^{22}Ne. A single barrier will enrich a constituent isotope of neon to the extent of $\sqrt{22/20} = 1.049$ which indeed is very small. This explains

TABLE : THE ISOTOPES OF NON-RADIOACTIVE ELEMENTS

Element	*At. No.*	*Isotopes*
H	1	1,2
He	2	3,4
Li	3	6,7
Be	4	9
B	5	10, 11
C	6	12, 13
N	7	14, 15
O	8	16, 17, 18
F	9	19
Ne	10	20, 21, 22
Na	11	23
Mg	12	24, 25, 26
Al	13	27
Si	14	28, 29, 30
P	15	31
S	16	32, 33, 34, 36
Cl	17	35, 37
A	18	36, 38, 40
K	19	39, 40*, 41
Ca	20	40, 42, 43, 46, 48
Sc	21	45
Ti	22	46, 47, 48, 49, 50
V	23	51
Cr	24	50, 52, 53, 54
Mn	25	55
Fe	26	54, 56, 57, 58
Co	27	57, 59
Ni	28	58, 60, 61, 62, 64
Cu	29	63, 65
Zn	30	64, 66, 67, 68, 70
Ga	31	69, 71
Ge	32	70, 72, 73, 74, 76
As	33	75
Se	34	74, 76, 77, 78, 80, 82
Br	35	79, 81
Kr	36	78, 80, 82, 83, 84, 86
Rb	37	85, 87*
Sr	38	84, 86, 87, 88
Y	39	89
Zr	40	90, 91, 92, 94, 96
Nb	41	93
Mo	42	92, 94, 95, 96, 97, 98, 100
Tc	43	99
Ru	44	96, (98), 99, 100, 101, 102, 104
Rh	45	101, 103
Pd	46	102, 104, 105, 106, 108, 110
Ag	47	107, 109
Cd	48	106, 108, 110, 111, 112, 113, 114, 116
In	49	113, 115
Sn	50	112, 114, 115, 116, 117, 118, 119, 120, 122, 124
Sb	51	121, 123
Te	52	120, 122, 123, 124, 125, 126, 128, 130
I	53	127
Xe	54	124, 126, 128, 129, 130, 131, 132, 134, 136
Cs	55	133
Ba	56	130, 132, 134, 135, 136, 137, 138
La	57	139
Ce	58	136, 138, 140, 142
Pr	59	141
Nd	60	142, 143, 144, 145, 146, 148, 150
Pm	61	147
Sm	62	144, 147, 148*, 149, 152, 154
Eu	63	151, 153
Gd	64	152, 154, 155, 156, 157, 158, 160
Tb	65	159
Dy	66	158, 160, 161, 162, 163, 164
Ho	67	165
Er	68	162, 164, 166, 167, 168, 170
Tm	69	169
Yb	70	168, 170, 171, 172, 173, 174, 176
Lu	71	175, 176*
Hf	72	(172), 174, 176, 177, 178, 179, 180
Ta	73	181
W	74	180, 182, 183, 184, 186
Re	75	185, 187*
Os	76	184, 186, 187, 188, 189, 190, 192
Ir	77	191, 193
Pt	78	192, 194, 195, 196, 198
Au	79	197
Hg	80	196, 198, 199, 200, 201, 202, 204
Tl	81	203, 205
Pb	82	204, 206, 207, 208
Bi	83	209

*These have weak radioactivity with long half-lives.

the necessity of continuous successive diffusions, often several hundred times. In 1932, Hertz employed a cascade of 48 diffusion pumps in series in a closed circuit and succeeded in obtaining a sample of neon with the composition 99% ^{20}Ne and 1% ^{22}Ne. The method has been employed in many other cases. By successive diffusions, hydrogen of mass 2 (*i.e.*, heavy hydrogen ^{2}H) was practically completely separated from the lighter isotope, the normal hydrogen, ^{1}H.

(*b*) *Thermal diffusion method.* In 1938, Clausius and Dickel used a 36-metre long vertical pipe with an electrically heated wire running down its axis to separate isotopes. The walls of the pipe were kept very cold. When a mixture of isotopes in gaseous form, is led in, thermal diffusion causes concentration of lighter component near the hot wire and the heavier component near to the cold walls. Moreover, due to thermal convection, the heavier component goes downwards along the cold wall while the lighter component goes up along the hot wire. Thus there are two streams moving in opposite directions having different proportions of a component isotope. With chlorine gas, practically a complete separation was possible with this method. The method has increasing applications now for its evident simplicity and effectiveness.

(*c*) *Evaporation method.* That the rates of evaporation of isotopic atom (or molecules) from a mixture are inversely proportional to the square roots of their masses has been taken advantage of in separating them. Lighter atoms would leave the surface more easily leaving the residue richer in heavier component. The evaporation has to be carried out at a very low pressure so that the atoms evaporated may not return to the surface. Bronsted and Hevesy and later Honigschmid and Birkenbach, distilling mercury at a low pressure successively obtained fractions differing appreciably in their densities. Keesom used this method in separating heavy hydrogen.

(*d*) *Electrolytic method.* Washburn and Urey (1932) found that water in the commercial electrolytic cell which was in use for several years had a higher density and in fact contained a greater proportion of ^{2}H, heavy hydrogen. During electrolysis of aqueous solution, the lighter isotope of hydrogen ^{1}H, is preferentially evolved (due to its low overvoltage) and the residual liquid contained a greater proportion of the heavier isotope, ^{2}H. Starting with 20 litres of water from old electrolytic cells, Lewis and Macdonald electrolysed it until the volume was reduced to 0.5 c.c. This residue was found to have a density of 1.073 containing nearly 70% of heavy water, ^2H_2O. Subsequently this electrolytic method has been employed on a commercial scale to produce almost pure heavy water, so necessary for controlling chain-fission of uranium. This is usually achieved by electrolysing 0.5 M NaOH solution with Ni-electrodes repeatedly.

(*e*) *Separation by exchange reaction.* Different isotopic species of an element exhibit the same chemical properties but the rates of a chemical process differ somewhat with the different species. In competing reactions, the heavier isotope reacts more slowly. This is particularly noticeable with isotopes of lighter elements. The difference in reactivity has been used in concentrating isotope with the help of *isotopic exchange reaction.* In such a reaction an isotope in one compound exchanges with another isotope of the same element in another compound. If the chemical reactivities of both the isotopes were the same, the equilibrium constant would be unity. But in actual experiments, the equilibrium constant is greater than unity. Urey and Thode concentrated ^{15}N by passing ammonia gas through ammonium nitrate solution trickling down a glass-bead-packed tower when an exchange of the following type took place:

$$\underset{\text{gas}}{^{15}NH_3} + \underset{\text{liq}}{^{14}NH_4^+} = \underset{\text{gas}}{^{14}NH_3} + \underset{\text{liq}}{^{15}NH_4^+}; \qquad K = 1.033$$

Evidently ^{15}N will increase in proportion in the solution. In fact a concentration of 70% ^{15}N could be obtained in the solution.

25.9. Isobars

Sometimes two different elements, obviously having different atomic numbers, may have the same atomic mass. These are said to be *isobars*.

Examples. (*i*) $^{64}_{28}Ni$, $^{64}_{30}Zn$ (*ii*) $^{86}_{36}Kr$, $^{86}_{38}Sr$

(*iii*) $^{40}_{18}A$, $^{40}_{19}K$ (*iv*) $^{110}_{48}Cd$, $^{110}_{46}Pd$; etc.

β-ray emission in radioactive disintegration will always give rise to isobars.

(*i*) $$^{234}_{90}U_{XI} \xrightarrow{\beta} {}^{234}_{91}U_{XII}$$

(*ii*) $$^{214}_{82}RaB \xrightarrow{\beta} {}^{214}_{83}RaC$$

25.10 Isotones

Sometimes two isotopes of two different elements (hence different atomic numbers) have the same number of neutrons in their nuclei. These are called *isotones*. Their atomic masses as well as their atomic number (proton numbers) are different, only the neutron number is same.

Examples. (*i*) $^{227}_{89}Ac$, $^{226}_{88}Ra$ (*ii*) $^{90}_{40}Zn$, $^{92}_{42}Mo$

(*iii*) $^{82}_{36}Kr$, $^{84}_{38}Sr$

25.11. Packing fraction

(*a*) *Whole number rule.* As long ago as 1815 Prout had suggested that all elements were built up out of hydrogen atoms associated in different numbers. The hypothesis was discarded when many atomic weights were found to be non-integral, such as Cl = 35.4. About a century later when isotopes were discovered the atomic masses were found to be nearly whole numbers. Thus, chlorine was found to be a mixture of atoms of masses 35 and 37. Neon (20.2) is a mixture of atoms having mass 20 and mass 22. Even elements whose atomic weight appeared to be integral were found to consist of minute proportion of isotopes. Oxygen

(16) is found to be really accompanied with 0.2% of oxygen mass 18 and 0.04% of oxygen mass 17.

On the nuclear theory of the atom, hydrogen atom has one proton and one electron, the mass of the latter is negligible. All other atoms have nuclei made up of protons and neutrons; the weight of a neutron is almost the same as that of a proton. Neglecting the mass of the electrons of the atom, its mass is thus an integral multiple of that of the hydrogen atom. Prout's hypothesis is therefore generally acceptable in a modified form.

(*b*) *Packing fraction*. With the use of mass spectrograph, very precise determination of atomic masses became possible. Aston found that in most cases there was a slight deviation from whole number for the mass of an isotope. The nearest integral number called the mass number (A) is indeed the sum total of the numbers of protons and neutrons. The deviation from the whole number varies from nucleus to nucleus and Aston expressed it in terms of *packing fraction* defined as

$$\text{packing fraction} = \frac{\text{isotope mass} - \text{mass number}}{\text{mass number}} \times 10^4$$

The packing fraction is often negative but sometimes positive also (Fig. XXV.4). Negative fraction implies stability of the nucleus while positive fraction indicates instability. Very light and very heavy elements have positive fractions while elements in the middle range have negative packing fraction. The chlorine isotope of mass 35 has the packing fraction,

$$10^4 \times \frac{(34.980 - 35.000)}{35.000} = -5.7$$

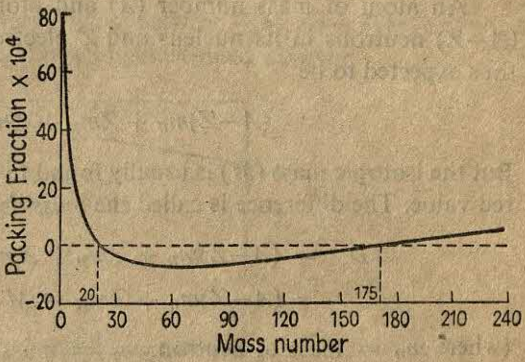


Fig. XXV. 4

(*c*) *Atomic mass unit*. There had been some difficulty in expressing the atomic masses in view of the uncertainty of the standard. The chemists expressed atomic weights taking naturally occurring oxygen, as the standard, O = 16.000 units. But it is now known that this oxygen is accompanied with two other isotopes, ^{17}O = 0.04% and ^{18}O = 0.2%. The atomic weight of ordinary oxygen in this scale would be

$$16.000 \times 0.9976 + 17.00450 \times 0.0004 + 18.00369 \times 0.002 = 16.0044$$

The ratio of physicists' to chemists' atomic wt. is thus 16.0044/16.000 = 1.000275. Since 1961, a unified standard has been accepted for atomic masses where the atomic mass of the carbon isotope ^{12}C has been fixed as 12.0000. In this scale, naturally occurring oxygen has the atomic weight O = 15.9999 and the isotope ^{16}O = 15.9949.

An atom of mass number 12 is our standard, hence one atomic mass unit (amu) is given by, (N_0 = Avogadro number),

$$1 \text{ amu} = \frac{1}{12} \cdot \frac{12 \text{ gm}}{N_0} = \frac{1}{6.025 \times 10^{23}} = 1.66 \times 10^{-24} \text{ gm}$$

TABLE : MASSES OF FUNDAMENTAL PARTICLES IN AMU SCALE

Units	*Symbol*	*Mass (amu)*	*Charge*
Proton	p	1.008142	+
Neutron	n	1.008983	0
Electron	e, β^-	0.000549	−
Deuteron	d	2.014190	+
α-particle	α	4.002770	+
H-atom	H	1.00814	0

25.12. Mass defect: Binding energy

An atom of mass number (A) and atomic number (Z) has Z protons and ($A-Z$) neutrons in its nucleus and Z electrons outside. The mass of the atom is thus expected to be

$$(A-Z)m_n + Zm_p + Zm_e$$

But the isotopic mass (M) is usually found to be less than the theoretically calculated value. The difference is called the *mass defect* (D);

$$\begin{aligned} D &= (A-Z)m_n + Zm_p + Zm_e - M \\ &= (A-Z)m_n + Zm_H - M \end{aligned}$$

(where m_n = mass of neutron, m_p = mass of proton, m_e = mass of electron, and mass of hydrogen atom, $m_H = m_p + m_e$)

It is now accepted that the energy required to hold together the constituent particles, protons, neutrons and electrons in the atom is derived from the loss of mass of the particles as measured by the mass defect. The mass lost is rendered into energy in accordance with the Einstein's principle of relativity, $E = mc^2$.

$\therefore$ One amu is $1.66 \times 10^{-24}(2.997 \times 10^{10})^2 = 1.492 \times 10^{-3}$ ergs

Since 1 electron volt (ev) = 1.6×10^{-12} ergs and 1 Mev = 10^6ev

We have $$1 \text{ amu} = \frac{1.492 \times 10^{-3}}{1.6 \times 10^{-12} \times 10^6} = 931 \text{ Mev}$$

The energy which is derived from the mass lost is responsible for holding the constituent particles together and is hence the *binding energy*, E_B. Expressed in Mev units, the binding energy in an atom is given by

$$E_B = 931 \times D = 931\,[(A-Z)m_n + Zm_H - M]$$

To illustrate: The mass defect in the deuterium atom (mass, 2.01474 amu) is

$$\begin{aligned} D &= m_p + m_n + m_e - m \\ &= 1.00814 + 1.00898 + 0.00055 - 2.01474 \\ &= 0.00293 \end{aligned}$$

Hence the binding energy, $E_B = 931 \times 0.00293 = 2.72$ Mev

The binding energy of an electron is only 14 ev, which is negligible compared to the total binding energy. The average binding energy per particle of this nucleus, *i.e.*, per nucleon, is 1.36 Mev. The mean binding energy per nucleon is different in different atoms. For example,

atom	*binding energy* (Mev)	*mean E_B per nucleon* (Mev)
^{7}Li	39.27	5.61
^{12}C	92.3	7.69
^{20}Ne	160.0	8.00
^{209}Bi	1630.0	7.80

Majority of the nuclei have binding energy lying between 7.5 and 8.5 Mev. In Fig. XXV.5, the mean binding energy is plotted against mass number.

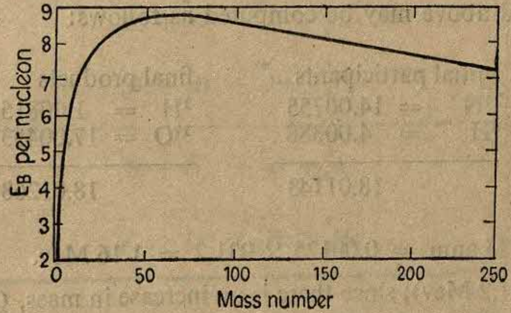


Fig. XXV.5. Binding energy and mass-number of atoms

The larger the mass defect, the larger would be the binding energy and more stable will be the nucleus.

25.13. Artificial Transmutation of Elements

The first act of disintegration of a stable element, nitrogen, by α-particle bombardment is attributed to Rutherford. When nitrogen nucleus is struck with α-particles, a nuclear reaction takes place producing oxygen and simultaneously ejecting a proton.

$$^{14}_{7}N + ^{4}_{2}He \rightarrow ^{17}_{8}O + ^{1}_{1}H$$

This is evidently a case of Nuclear transformation due to bombardment by a projectile (α-particle). One element thus undergoes transmutation into another.

In 1936, Bohr suggested that such transformations are two-stage processes. A compound nucleus comprising the projectile and the target nucleus is first formed which has a very short life-time.

The compound nucleus subsequently splits down to new products in ways which are energetically feasible. The atomic number of the compound nucleus must be the sum of the atomic numbers of the target nucleus and the projectile. The compound nucleus would therefore represent an isotope of the element which has the 'added' value as atomic number. The transmutation of nitrogen, mentioned earlier may now be expressed as:

$$\overset{14}{{}_7N} + \overset{4}{{}_2He} \rightarrow \left(\overset{18}{{}_9F}\right) \rightarrow \overset{17}{{}_8O} + \overset{1}{{}_1H} + Q$$

The compound nucleus is that of a flourine isotope having atomic number $7 + 2 = 9$. The mass number of the compound nucleus is the sum of the mass numbers of the initial particles, and also the sum of the mass numbers of the final products. The constancy of mass numbers is true but the total atomic masses would not remain constant, for atomic masses are slightly different from mass numbers. When the total atomic mass of the products is less than that of the initial participants, an energy Q will be given out, governed by the relation, $mc^2 = \epsilon$. The value of Q will be negative *i.e.*, energy will be absorbed when the total mass of the products is more than that of the initial reactants. The value of Q in the transmutation cited above may be computed as follows:

Initial participants	final products
$^{14}N = 14.00755$	$^{1}H = 1.00815$
$^{4}H = 4.00388$	$^{17}O = 17.00453$
18.01143	18.01268

$$\Delta m = 0.00125 \text{ amu} = 0.00125 \times 931.2 = 1.16 \text{ Mev.}$$

(1 amu = 931.2 Mev); since there is an increase in mass, $Q = -1.16$ Mev.

This corresponds satisfactorily to experimental measurements of kinetic energies.

In this transformation, the projectile is an α-particle (α) and the ejected particle is a proton (p). This is indicated as an (α, p) type of transformation. Other (α,p) types of transmutation are

$$\overset{27}{{}_{13}Al} + \overset{4}{{}_2He} \rightarrow \left(\overset{31}{{}_{15}P}\right) \rightarrow \overset{30}{{}_{14}Si} + \overset{1}{{}_1H} \; ; Q = +2.26 \text{ Mev.}$$

$$\overset{39}{{}_{19}K} + \overset{4}{{}_2He} \rightarrow \left(\overset{43}{{}_{21}Sc}\right) \rightarrow \overset{42}{{}_{20}Ca} + \overset{1}{{}_1H}; \; Q = -0.89 \text{ Mev.}$$

There are various other artificial transmutations carried out in which missiles other than α-particles are used, such as (*i*) neutrons (*ii*) protons (*iii*) deuterons (*iv*) γ-rays. In these nuclear reactions (excluding fission type reactions), when bombardment energy is in the range 0–10 Mev, γ-rays, protons, neutrons and α-particles may be ejected. Very high-energy projectiles (100–400 Mev) cause *spallation, i.e.*, an event in which many nucleons and groups are simultaneously given out.

A few examples of different types of transmutation are given here:

Projectile	*Transmutation*	*Type*
α	${}^{7}_{3}\mathrm{Li} + {}^{4}_{2}\mathrm{He} \rightarrow {}^{10}_{5}\mathrm{B} + {}^{1}_{0}\mathrm{n}$	(α, n)
	${}^{11}_{5}\mathrm{B} + {}^{4}_{2}\mathrm{He} \rightarrow {}^{14}_{7}\mathrm{N} + {}^{1}_{0}\mathrm{n}$	(α, n)
n	${}^{27}_{13}\mathrm{Al} + {}^{1}_{0}\mathrm{n} \rightarrow {}^{24}_{11}\mathrm{Na} + {}^{4}_{2}\mathrm{He}$	(n, α)
	${}^{56}_{20}\mathrm{Fe} + {}^{1}_{0}\mathrm{n} \rightarrow {}^{56}_{25}\mathrm{Mn} + {}^{1}_{1}\mathrm{H}$	(n, p)
	${}^{39}_{19}\mathrm{K} + {}^{1}_{0}\mathrm{n} \rightarrow {}^{38}_{19}\mathrm{K} + 2\,{}^{1}_{0}\mathrm{n}$	$(n, 2n)$
p	${}^{7}_{3}\mathrm{Li} + {}^{1}_{1}\mathrm{H} \rightarrow 2\,{}^{4}_{2}\mathrm{He}$	(p, α)
	${}^{12}_{6}\mathrm{C} + {}^{1}_{1}\mathrm{H} \rightarrow {}^{13}_{7}\mathrm{N} + \gamma$	(p, γ)
d	${}^{27}_{13}\mathrm{Al} + {}^{2}_{1}\mathrm{D} \rightarrow {}^{28}_{14}\mathrm{Si} + {}^{1}_{0}\mathrm{n}$	(d, n)
	${}^{9}_{4}\mathrm{Be} + {}^{2}_{1}\mathrm{D} \rightarrow {}^{10}_{4}\mathrm{Be} + {}^{1}_{1}\mathrm{H}$	(d, p)
γ	${}^{2}_{1}\mathrm{H} + h\nu \rightarrow {}^{1}_{1}\mathrm{H} + {}^{1}_{0}\mathrm{n}$	(γ, n)
	${}^{12}_{6}\mathrm{C} + h\nu \rightarrow {}^{8}_{4}\mathrm{Be} + {}^{4}_{2}\mathrm{He}$	(γ, α)

Problem. Calculate the Q value for the formation of ${}^{31}\mathrm{P}$ in the ground state in the reaction, ${}^{30}\mathrm{Si}\,(d, n)\,{}^{31}\mathrm{P}$. Given

(*a*) ${}^{30}\mathrm{Si} + d \rightarrow {}^{31}\mathrm{Si} + p + 4.367$ Mev
(*b*) ${}^{31}\mathrm{Si} \rightarrow {}^{31}\mathrm{P} + \beta + 1.51$ Mev
(*c*) $n \rightarrow p + \beta + 0.782$ Mev.

Adding (*a*) and (*b*) and subtracting (*c*) we have

${}^{30}\mathrm{Si} + d = {}^{31}\mathrm{P} + n + (4.367 + 1.51 - 0.782)$ Mev

Hence $Q = 5.095$ Mev

25.14. Artificial Radioactivity

The artificial production of elements possessing radioactivity had its beginning in the experiments of Frederik Joliot and Irene Joliot-Curie while studying the effect of α-impingement on metallic aluminium. The artificial disintregation of aluminium by α-particles leads to the production of silicon accompanied by proton emission.

$$^{27}_{13}\mathrm{Al} + {}^{4}_{2}\mathrm{He} \rightarrow {}^{30}_{14}\mathrm{Si} + {}^{1}_{1}\mathrm{H}$$

It was found by the Joliot couple that in addition to proton emission, this disintegration is also accompanied with neutron and positron emission and that while proton and neutron emission ceased as soon as α-irradiation was stopped, the positrons continued to be emitted. An immediate explanation for the phenomenon was offered. The artificial disintegration of aluminium by α-particles proceeds in two ways, one of which follows the pattern shown above. In another way, α-bombardment first produces an unstable isotope of phosphorus with the ejection of a neutron. This unstable phosphorus nucleus is radioactive and decays into silicon with the emission of a positron.

$$\begin{array}{l} {}^{27}_{13}\mathrm{Al} + {}^{4}_{2}\mathrm{He} \rightarrow {}^{30}_{15}\mathrm{P}^{*} + {}^{1}_{0}n \\ \qquad\qquad\qquad\quad \downarrow \\ \qquad\qquad\qquad\quad {}^{30}_{14}\mathrm{Si} + {}^{0}_{1}e^{+}\ \text{(positron)} \end{array}$$

This was the first instance of the discovery of induced radioactivity where a stable non-radioactive nucleus after transmutation was rendered radioactive. This was soon followed by a spate of discoveries of other artificially produced radioactive isotopes such as (the asterisk indicates the artificial radioactive species),

$$\begin{array}{l} {}^{24}_{12}\mathrm{Mg} + {}^{4}_{2}\mathrm{He} \rightarrow {}^{27}_{14}\mathrm{Si}^{*} + {}^{1}_{0}n \\ \qquad\qquad\qquad\quad \downarrow \\ \qquad\qquad\qquad\quad {}^{27}_{13}\mathrm{Al} + {}^{0}_{1}e^{+} \end{array} \qquad \begin{array}{l} {}^{10}_{5}\mathrm{B} + {}^{4}_{2}\mathrm{He} \rightarrow {}^{13}_{7}\mathrm{N}^{*} + {}^{1}_{0}n \\ \qquad\qquad\qquad\quad \downarrow \\ \qquad\qquad\qquad\quad {}^{12}_{6}\mathrm{C} + {}^{0}_{1}e^{+} \end{array}$$

The artifiicial radioactive elements behave in the same fashion as the naturally radioactive ones. The decay of these elements follows the same first order law.

Not only α-particles but other accelerated particles like protons, deuterons or neutrons are now extensively used to obtain artificially radioactive elements. Some examples are given here. Usually, the artificially radioactive species emits either electron or positron.

$$(a)\ \begin{array}{l} {}^{27}_{13}\mathrm{Al} + {}^{1}_{0}n \rightarrow {}^{24}_{11}\mathrm{Na}^{*} + {}^{4}_{2}\mathrm{He} \\ \qquad\qquad\qquad\quad \downarrow \\ \qquad\qquad\qquad\quad {}^{24}_{12}\mathrm{Mg} + {}^{0}_{1}e^{-} \end{array} \qquad (b)\ \begin{array}{l} {}^{31}_{15}\mathrm{P} + {}^{1}_{0}n \rightarrow {}^{31}_{14}\mathrm{Si}^{*} + {}^{1}_{1}\mathrm{H} \\ \qquad\qquad\qquad\quad \downarrow \\ \qquad\qquad\qquad\quad {}^{31}_{15}\mathrm{P} + {}^{0}_{1}e^{-} \end{array}$$

$$(c)\ {}^{127}_{53}\mathrm{I} + {}^{1}_{0}n \rightarrow {}^{128}_{53}\mathrm{I}^{*} \rightarrow {}^{128}_{54}\mathrm{Xe} + {}^{0}_{1}e^{-}$$

$$(d)\ \begin{array}{l} {}^{85}_{37}\mathrm{Rb} + {}^{1}_{0}n \rightarrow {}^{84}_{37}\mathrm{Rb}^{*} + 2{}^{1}_{0}n \\ \qquad\qquad\qquad\quad \downarrow \\ \qquad\qquad\qquad\quad {}^{84}_{38}\mathrm{Sr} + {}^{0}_{1}e^{-} \end{array} \qquad (e)\ \begin{array}{l} {}^{39}_{19}\mathrm{K} + {}^{1}_{0}n \rightarrow {}^{38}_{19}\mathrm{K}^{*} + 2{}^{1}_{0}n \\ \qquad\qquad\qquad\quad \downarrow \\ \qquad\qquad\qquad\quad {}^{32}_{18}\mathrm{A} + {}^{0}_{1}e^{+} \end{array}$$

25.15. Nuclear Fission

It was in 1939 Otto Hahn and S. Strassmann, from a very careful set of experiments and the analysis of the results of the same, established that one of the products of neutron irradiation of uranium was an isotope of Barium (at. no. 56). The other nucleus produced was thus considered to be krypton (at. no. 36). This was an astounding observation. Before this, all the transmutations known—natural and artificial—involved small changes in mass or in atomic numbers; in those changes either there was an increment in mass by absorption of a particle or there would be a decrease due to emission of a particle. It was the first instance of a major rupture of a heavy nucleus into fragments having atomic masses of medium sizes. Such disintegrations in which a heavy nucleus breaks up into two nuclei of comparable masses are called '*nuclear fissions*'.

Further probe into the splitting of uranium by neutron bombardment revealed that among the different isotopes of uranium, it was ^{235}U which was most readily fissionable. The rupture takes place as follows:

$$^{235}_{92}U + ^{1}_{0}n \rightarrow \left(^{236}_{92}U\right) \rightarrow ^{141}_{56}Ba + ^{92}_{36}Kr + 3\,^{1}_{0}n + Q \qquad \ldots (1)$$

Careful experimental observations have brought out a number of facts which, shorn of details, may be summarised below:

(*a*) In the process of nuclear fission a large amount of energy is released which is considerably greater than that evolved in any other process. The number of nucleons before and after the process remains the same, but the sum of the mass of the fragments and released neutrons is less than the mass of the disintegrating U-atom and the projectile neutron. An approximate calculation, with Einstein's equation $\epsilon = mc^2$, in the above process shows that there would be a mass defect of about 0.215 amu which is equivalent to about 200 Mev. This indeed is a very large quantity of energy. It became immediately evident that such fission would be a source of enormous power.

(*b*) Fission of each uranium nucleus is accompanied by release of $2 \sim 3$ neutrons. These neutrons, under suitable conditions, bombard fresh uranium atoms splitting them and producing more neutrons. Thus a chain reaction of splitting would ensue and its propagation would rapidly increase. At each step considerable energy would be released.

(*c*) ^{235}U undergoes fission both by fast as well as slow neutrons, though the latter are more effective in carrying out the rupture. The main isotope ^{238}U, in general, absorbs slow neutrons but instead of undergoing fission, it yields transuranic elements (Np and Pu) as follows:

$$^{238}_{92}U + ^{1}_{0}n \rightarrow \left(^{239}_{92}U\right) \rightarrow ^{239}_{93}Np + ^{0}_{1}e^{-} \quad (t_{\frac{1}{2}} = 23 \text{ min})$$

$$^{239}_{93}Np \rightarrow ^{239}_{94}Pu + ^{0}_{1}e^{-} \quad (t_{\frac{1}{2}} = 2.3 \text{ days}) \qquad \ldots (II)$$

That is, with slow neutron bombardment, ^{238}U is first transformed into the element ($Z = 93$) called neptunium. This is radioactive and spontaneously disintegrates into the next element plutonium ($Z = 94$) with β-ray emission.

(*d*) Plutonium formed from uranium by β-emissions (see II above) is fissionable like ^{235}U. It has comparatively a long half-life period and can thus be stored in quantities. The isotope ^{235}U occurs in low amounts in uranium minerals [$^{238}U/^{235}U = 140$], and its separation from the abundant isotope ^{238}U is rather hard. Plutonium has thus proved to be the chief source of atomic energy both for peaceful uses as well as for destructive purposes including the nuclear bomb.

Atomic Bomb. On bombarding ^{235}U with neutrons, for every single fission approximately 200 Mev energy is released. The process yields moreover 3 new neutrons on an average, each in its turn leads to the fission of fresh ^{235}U. At every stage, in this way, the energy output will multiply and the cumulative effect of even one initial fission would be enormous. The chain would continue if the piece of ^{235}U taken is large enough and the secondary neutrons produced find targets. If the piece of ^{235}U is small, the neutrons produced will escape and the chains will break up. There is thus a limiting or critical size of the target for intense production of energy by chain propagation. If the size is below the critical limit, there will be no explosion and the process is safe. A larger piece from which the secondary neutrons cannot escape will cause the explosion.

It has been estimated that on the capture of a neutron by a fissile ^{235}U, the secondary neutrons are expelled in about 10^{-14} sec. And the average time required for the capture of a secondary neutron by the target nuclei is about 10^{-8} sec.

The total output of energy when 1 Kg ^{235}U is exposed to neutron bombardment is about 2.2×10^7 KWH.

This energy appears within 10^{-6} sec as heat in the uranium from which the fission products cannot escape. It produces a tremendous explosion resulting into a violent blast and an intense temperature of 10^7 °K, associated with dangerous radioactivity. It is necessary that ^{235}U should be pure. The presence of ^{238}U or other materials will absorb the neutrons and break the chain.

In fact, in the actual operation two rods of ^{235}U, each below the critical size, are taken and at the desired moment the two pieces are brought together to exceed the critical size and cause the explosion. Though earlier tests were made, the first effective bomb, called the 'lean boy', was released on Hiroshima at 8.11 A.M. on August 5, 1945 from an altitude of 31600 feet. The bomb had two blocks of ^{235}U enclosed at the two ends of a barrel. The two sections were brought together at the right moment to exceed the critical size. The effects are known to every human being now.

Nuclear Reactors or Atomic Piles. The longer the chain propagation in a fission process the greater will be the explosive power of an atom bomb. But in such cases, the energy, though vast, cannot be used for any peaceful purpose. The useful application of the fission energy rests on the proper control of the propagation of the chain. This is achieved with what is commonly called 'an atomic pile or a nuclear reactor'. The reactor is indeed an arrangement of nuclear fuel (^{235}U or Pu etc.), together with other materials which act as moderators, to enable a proper control of the self-sustaining chain reaction. In such a controlled fission not only the explosive tendencies are avoided, but the ractors function (*i*) in supplying slow or fast neutrons, (*ii*) in producing radioactive nuclides, *e.g.*, Pu, and (*iii*) in liberating heat energy that could be used to drive turbo-generators for electric power production.

To sustain a chain reaction in a fission process, the minimum requirement is that each nucleus undergoing fission must produce, on the average, at least one neutron to effect another fission. The number of neutrons resulting from a single fission is known as the *reproduction factor*. If this number be less than unity, chain reaction is not possible. When the factor is greater than unity, the chain reaction might continue. In the reactor the atomic fuels and moderator are so arranged that the reproduction factor is carefully controlled to a value equal to unity or slightly greater than unity. Rods of natural uranium containing both ^{238}U and ^{235}U are taken. The total uranium taken should exceed the critical size. in order to allow the chain reaction to proceed. But the chain is controlled by inserting between the uranium rods blocks of substances like cadmium, coke, etc. which absorbs the neutrons. The rods can be moved in or out according to necessity.

25.16. Nuclear Fusion

The energy released in the fission of nuclei originates from the loss of mass occurring in the process. On the other hand, when very light nuclei would join or *fuse* together, there would be a loss in mass. For example if two protons and two neutrons would fuse, or if two deuterons would unite, the loss in mass would be as follows:

$$\begin{array}{ccccc} 2\,{}^{1}_{1}\mathrm{H} & + & 2\,{}^{1}_{0}n & \rightarrow & {}^{4}_{2}\mathrm{He}\ ; \qquad \Delta m \\ 2\times1.00814 & & 2\times1.00898 & & 4.00388\ ;\ \ 0.03424\ \text{amu} \approx 28\ \text{Mev} \end{array}$$

$$\begin{array}{ccc} 2\,{}^{2}_{1}\mathrm{H} & \rightarrow & {}^{4}_{2}\mathrm{He} \\ 2\times2.01471 & & 4.00388\ ; \qquad 0.02554\ \text{amu} \approx 24\ \text{Mev} \end{array}$$

That means, such a fusion process would lead to liberation of energy. But the real difficulty in effecting such a fusion arises from the intense repulsion between the positive nuclei. If however the temperature could be raised very high the repulsion might be overcome by the increase in kinetic energy of the nuclei. Calculation shows that the temperature required would be of the order of $10^6 \sim 10^7$ °K. Such high temperatures can be attained terrestrially only in a fission reaction. Thus if plutonium or ^{235}U be allowed to undergo fission in an explosive chain reaction in an abundance of portons or other hydrogen isotopes, the temperature would be high enough to initiate fusion processes amongst the latter. The momentary high temperature would provide the nuclei of lighter elements with enough kinetic energy to penetrate into each other and fuse. Since very high temperature exists for a brief lapse of time, only such nuclear fusions which proceed with extraordinary rapidity can happen.

It is believed that such conditions have been attained in the creation of thermonuclear bombs, such as the *hydrogen bomb*. The exact fusion reactions for the hydrogen bomb have not been revealed, but it is generally thought the tritium and deuteron or proton are involved in the process. The transformation would be of the type:

$${}^{3}_{1}\mathrm{H} + {}^{2}_{1}\mathrm{H} \rightarrow {}^{4}_{2}\mathrm{He} + {}^{1}_{0}n + 17\ \text{Mev}$$

$${}^{3}_{1}\mathrm{H} + {}^{1}_{1}\mathrm{H} \rightarrow {}^{4}_{2}\mathrm{He} + 20\ \text{Mev}$$

$$ {}^{3}_{1}\mathrm{H} + {}^{3}_{1}\mathrm{H} \rightarrow {}^{4}_{2}\mathrm{He} + 2\,{}^{1}_{0}n + 11\ \text{Mev. etc.} $$

In the bomb, probably there is a small core of plutonium fission bomb to act as detonator. This is surrounded by thick cover of fusible material, which in turn is enclosed by natural uranium. The fast neutrons produced in fusion leads to the fission of the surrounding uranium. The fusion process is not governed by critical size limit, very large hydrogen bombs can therefore be produced. The results of the explosion of such devices are stupendous and frightening.

Sometimes an electron from the *K*-shell is drawn into the nucleus. In consequence an electron from the higher energy level drops into the *K*-shell to replace the captured electron. This is often called *K*-**capture.** When the electron from the higher level drops into the *K*-level, radiations are emitted.

25.17. Transuranic Elements

In the original periodic table, the heaviest element was Uranium (at. no. 92). Starting from 1940, it has been possible to synthesise a series of new heavier elements having at. no. (93 ~ 105). All of them are, of course, radioactive. These form the 'Actinide Series' corresponding to the Lanthanide series. We have already mentioned earlier how Neptunium (93) and plutonium (94) were prepared by neutron bombardment of Uranium. In the sythesis of others, not only α-particles but ions of boron, carbon, nitrogen etc. were also used. Some of these transmutation processes are indicated below:

missile	*Process*	*Type*
	${}^{241}_{94}\mathrm{Pu} \rightarrow {}^{241}_{95}\mathrm{Am} + {}^{0}_{1}e^{-}$	β-decay
α	${}^{239}_{94}\mathrm{Pu} + {}^{4}_{2}\mathrm{He} \rightarrow {}^{241}_{96}\mathrm{Cm} + 2\,{}^{1}_{0}n$	(α, 2*n*)
α	${}^{241}_{95}\mathrm{Am} + {}^{4}_{2}\mathrm{He} \rightarrow {}^{243}_{97}\mathrm{Bk} + 2\,{}^{1}_{0}n$	(α, 2*n*)
α	${}^{242}_{96}\mathrm{Cm} + {}^{4}_{2}\mathrm{He} \rightarrow {}^{244}_{98}\mathrm{Cf} + 2\,{}^{1}_{0}n$	(α, 2*n*)
C-nuclei	${}^{238}_{92}\mathrm{U} + {}^{12}_{6}\mathrm{C} \rightarrow {}^{246}_{98}\mathrm{Cf} + 4\,{}^{1}_{0}n$	(*C*, 4*n*)
N-nuclei	${}^{238}_{92}\mathrm{U} + {}^{14}_{7}\mathrm{N} \rightarrow {}^{247}_{99}\mathrm{Es} + 5\,{}^{1}_{0}n$	(*N*, 5*n*)
O-nuclei	${}^{238}_{92}\mathrm{U} + {}^{16}_{8}\mathrm{O} \rightarrow {}^{250}_{100}\mathrm{Fm} + 4\,{}^{1}_{0}n$	(*O*, 4*n*)
α	${}^{253}_{99}\mathrm{Es} + {}^{4}_{2}\mathrm{He} \rightarrow {}^{256}_{101}\mathrm{Md} + {}^{1}_{0}n$	(α, *n*)
C-nuclei	${}^{246}_{96}\mathrm{Cm} + {}^{12}_{6}\mathrm{C} \rightarrow {}^{254}_{102}\mathrm{No} + 4\,{}^{1}_{0}n$	(*C*, 4*n*)

The eleven transuranic elements born during 1940 ~ 61 are listed below with their atomic mass numbers.

TRANSURANIC ELEMENTS

Name		At. no.	atomic mass number	Name		At. no.	atomic mass number
Neptunium	(Np)	93	231–241	Einsteinium	(Es)	99	246–256
Plutonium	(Pu)	94	232–243	Fermium	(Fm)	100	250–256
Americium	(Am)	95	237–244	Mendelevium	(Md)	101	256* ~
Curium	(Cm)	96	238–345	Nobelium	(No)	102	251* ~
Berkelium	(Bk)	97	243–245	Lawrencium	(Lc)	103	*
Californium	(Cf)	98	244–246				

(*range not definitely established)

25.18. Use of Isotopes

The outstanding achievement of the study of nuclear reactions and the isotopes is in the (*i*) prodution of energy through reactor (*ii*) synthesis of transuranic elements and (*iii*) discovery of the elements in the gaps of the periodic table. A few other typical applications will be mentioned here.

Medicinal use. The diagnostic and therapeutic use of isotopes in the field of medicine is now well-known. Radium, for some years now, was often employed in the treatment of cancer. For some of the undesirable effects of its decay products it is now being slowly replaced by ^{60}Co. The isotope ^{131}I is employed in the treatment of hyperthyroidism. ^{32}P or radiophosphorus is being used in some diseases of the blood by measuring its uptake in the bones.

Tracer Technique. If, in some of the molecules of a substance, one of the constituent atoms of its molecules be of radioisotopic variety, these molecules are said to be labelled or tagged. The proportion of the tagged molecules may be quite small in the whole mass of the substance. The chemical and physiological properties of the normal molecules and those with isotopic constituent are the same. The isotopic variety can be easily and readily detected from its radioactivity with a G-M counter. The element whose radioisotope is introduced is called the '*tracer element*'. By measuring its radioactivity, through the chemical or the physiological process, the fate of the substance at different stages can be discerned. Such a procedure reveals the course, progress and mechanism of a change and it is called 'tracer technique'. The technique is now widely employed and it solves many problems where other methods fail.

If in a stable phosphatic fertiliser, some amount of the same fertiliser prepared from ^{32}P be added and used. The uptake of phosphates by the plant or its lodging can be easily followed.

Suppose a small amount of acetic acid synthesised with ^{14}C in its methyl group, is added to the stable acetic acid, which is used in physiological system where it yields carbon dioxide. If the collected CO_2 does not show any radioactivity it is obvious that it is the carbonyl group which has participated in the process.

Batches of rats were fed with diet containing ^{32}P. At different time intervals, bone ash were tested for radioactivity. The results confirmed that a given phosphorus atom remained in the bones for about four weeks and were in eqm. with surroundings. Similarly, sodium chloride solution, tagged with ^{24}Na, injected in blood was followed to find out the rate and directions of circulation. Innumerable other applications are now being made.

Radiocarbon Dating. W. F. Libby suggested that the age of old samples containing carbon could be found out by determining ${}^{14}C$ content of the same. In the upper reaches of the atmosphere ${}^{14}C$ is being continuously synthesised at a *steady* rate by the action of neutrons of cosmic rays on stable ${}^{14}N$.

$$ {}^{14}_{7}N + {}^{1}_{0}n \rightarrow [{}^{15}_{7}N] \rightarrow {}^{14}_{6}C + {}^{1}_{1}H $$

The radio carbon thus formed is converted into carbon dioxide and is ultimately locked in the plants. Animals taking up the plants also contain ${}^{14}C$ in their tissues. The amount of ${}^{14}C$ present in these systems is about 1×10^{-12} per atom of ordinary carbon. ${}^{14}C$ has a half-life of 5568 years. Hence its activity would be 25% after nearly 11000 years.

Suppose now a sample had been first formed t years ago, then its present ${}^{14}C$ activity (I_t) is related to its initial activity (I_0) as

$$ I_t = I_0 e^{-\lambda t}, \quad \text{where } \lambda = 0.693/5568 \text{ years}^{-1} $$

By measuring the radioactivity of plant samples freshly formed, I_0 is obtained, remembering that the the rate of synthesis of ${}^{14}C$ is constant. The value is found as 15.3 counts per gm per minute. The present-day radioactivity (I_t) is measured with the sample. It is thus possible to find out t, the age of the sample. In this way samples as old as 25000 years can be dealt with.

Age of the Earth. The earth must be as old as the oldest mineral that can be detected. Applying radioactive methods, the age of some of the minerals could be fixed and found to be several thousand million years. The method is simple. The end products in the disintegration of uranium and thorium minerals is lead. The estimation of lead in such an undisturbed ore today determines the amount of uranium (q_2) which has suffered disintegration since its formation. Further, measurement of the present-day radioactivity of uranium in the ore can also be experimentally determined by analytical methods. Let the a mount of uranium present now be q_1. Then, the original amount of uranium was $(q_1 + q_2)$. From Rutherford's equation,

$$ N_t = N_0 e^{-\lambda t}, \quad \text{we have, } q_1 = (q_1 + q_2) e^{-\lambda t} $$

where $\lambda = 0.693/(4.6 \times 10^9) \text{ years}^{-1}$.

The age of the mineral (t years) is calculated and found to be 4.5×10^9 years.

EXERCISES

1. What are the types of radiations given off by radioactive substances?

How does the emission of each one of them affect the nucleus undergoing change? What is the law governing the rate of radioactive change? (*Delhi B.Sc.*)

2. Calculate the mass number, atomic number and group in the periodic table for Bi in the following disintegration sequences;

$$ {}^{226}_{88}Ra \xrightarrow{\alpha} Rn \xrightarrow{\alpha} Po \xrightarrow{\alpha} RaB \xrightarrow{\beta} Bi $$

Radium belongs to Group IIA. (*Allahabad B.Sc.*)

3. What is meant by the half-life period of a radioactive element? (*Delhi B.Sc., Calcutta B.Sc., Madras B.Sc.*)

4. Define half-life period and average life of a radioactive element.

The half-life period of carbon 14 is 5760 years. An old piece of wood in a museum has a disintegration rate which is 25% of the disintegration rate of an equal weight of new piece of wood. What is the age of the old piece of wood? (*Kurukshetra B.Sc.*) [Ans. 11520 Yr]

5. Write short notes on: (*i*) Group displacement law (*ii*) Artificial radioactivity (*iii*) Nuclear fission (*iv*) Nuclear binding energy.

6. Write what you know about the discovery of artificial radioactivity. How are the artifiical radioactive elements produced? Give the nuclear reactions. (*Viswabharati B.Sc.*)

7. Deduce the expression for the average life of a radioactive element. The disintegrated concentration of 7.5 moles of a radioactive substance was found to be 5 moles after 925 hours. Find its average life. (*Punjabi B.Sc.*) [Ans. 95.06 years]

8. Explain what are meant by radioactive constant, half-life and average life, as applied to radioactive elements. How are they related to one another?

At radioactive eqm, the ratio between atoms of two radioactive elements A and B was found to be $3.1 \times 10^{9} : 1$. If the half-life period of A is 2×10^{10} years, what is the half-life period of element B? (*Mysore B.Sc.*) [Ans. 6.452 years]

9. The amount of ^{14}C in a piece of fossil wood is found to be one-sixth of its amount in a fresh piece of wood. Show that the age of the fossil is 20170 years. (The half-life of ^{14}C is 5577 years.)

10. How many α- and β-particles are emitted when an atom of ${}^{232}_{90}Th$ disintegrates to ${}^{208}_{82}Pb$? [Ans. 6 α-particles; 4 β-particles]

11. Mention the important uses of radioactive isotopes. Illustrate with examples the use of tracers for analytical and for physiological investigations.

12. A radioactive substance has $t_{\frac{1}{2}} = 53300$ seconds. Show that its activity will fall to one-tenth of its original value in 2950 min.

13. The atomic mass (A) of Thorium is 232.12 and its atomic number (Z) is 90. Six α- and four β-particles are emitted when it disintegrates finally to non-radioactive end-product. Show that the end product has an atomic mass 208.12 amu and atomic number of 82.

14. Solve X in the following:

(*a*) ${}^{7}_{3}Li(p, n)X$; (*b*) ${}^{4}_{2}He + {}^{9}_{4}Be \rightarrow {}^{12}_{6}C + X$; (*c*) ${}^{55}Mn\,(n, X)\,{}^{56}Mn$;

(*d*) $2\,{}^{2}_{1}D \rightarrow {}^{3}_{2}He + X$; (*e*) ${}^{43}_{20}Ca\,(\alpha, p)\,X$

15. In what time will ^{24}Na lose its activity by 80% if its half-life be 15 hours?

16. ^{90}Y has a half-life of 64 hours and ^{90}Sr 28 years. ^{90}Sr decays to ^{90}Y by β-emission. What will be the amount of ^{90}Y in equilibrium with 1 gm of ^{90}Sr.

17. In a sample of pitchblende the atomic ratio $^{206}Pb : ^{238}U = 0.23 : 1$. Calculate the age of the mineral, if half-life of uranium is taken as 4.5×10^{9} years. All lead originated from uranium.

18. How many atoms of ^{14}C on an average are required to have ten β-emissions per minute? ^{14}C atoms have a half-life of 5600 years. [Ans. 4.25×10^{10} atoms]

CHAPTER 26

THE CHEMICAL BONDING

The ideas about valency were previously based on the observation of the chemical behaviour and composition of the molecules. The development of the theory of valency in the beginning was not made with the understanding of the nature of forces which caused different types of union between atoms or the arrangement of atoms in the molecule. The knowledge of electronic configuration of atoms in the beginning of this century gave a new and reasonable interpretation of bonding between atoms and the affinities exerted by atoms in their union. This is often mentioned as the *electronic theory of valency.*

We have seen in the previous chapter that the extraordinary stability of inert gases is due to their stable electronic configuration; all the inert gases have eight electrons in their outermost orbit. The elements which immediately precede an inert gas in the periodic table, namely the halogens, are all strongly electronegative and univalent. The elements which immediately follow the inert gases in the table, *i.e.*, the alkali metals, are all strongly electropositive and univalent. It was suggested that the atoms of different elements would always try to acquire a stable configuration of eight electrons in their outermost shell, akin to that of the inert gases. This is the fundamental principle of the electronic theory of valency commonly known as the *Octet Rule*. The achievement of stable configuration is possible mainly in two ways. Basically there are two extreme cases of chemical bonding and compounds are characterised either by one or the other and in many cases by an admixture of the two. These two extreme nature of bonding—*Ionic and Covalent*—should therefore be treated separately.

ELECTROVALENCY

26.1. The Ionic Bond

The electronic configurations of the halogens and of the alkali metals *vis-a-vis* the inert gases are :

Halogens	*Inert gases*	*Alkali metals*
F (2, 7)	Ne (2, 8)	Na (2, 8, 1)
Cl (2, 8, 7)	A (2, 8, 8)	K (2, 8, 8, 1)
Br (2, 8, 18, 7)	Kr (2, 8, 18, 8)	Rb (2, 8, 18, 8, 1)
I (2, 8, 18, 18, 7)	Xe (2, 8, 18, 18, 8)	Cs (2, 8, 18, 18, 8, 1)

Every halogen atom has seven electrons in its outermost orbit and would need only one electron to attain the stable configuration of the nearest inert gas, with eight electrons in outermost orbit. On the other hand, every alkali metal has one electron in the outermost orbit which it would try to part with in order to attain for itself a stable configuration. Kossel (1916) developed the theory that in the formation of molecules like KCl, which readily ionise and conduct electricity in solutions a transfer of electron occurs from one atom to another producing stable configurations. Thus, when a potassium atom unites with a chlorine atom, the former readily parts with its outermost electron and the latter takes up the same. The potassium atom becomes positively charged K^+ ion with a stable structure, while the chlorine atom is rendered into negatively charged Cl^- ion also with a stable structure. The two oppositely charged ions remain associated together by electrostatic forces to constitute the molecule. It means that in the formation of KCl molecule transfer of electron takes place from one atom to the other. The ions would separate from one another under suitable conditions, say, in a solution.

$$\begin{array}{ccccccc} K & + & Cl & = & [K^+] & & [Cl^-] \\ (2,8,8,1) & & (2,8,7) & & (2,8,8) & & (2,8,8) \end{array}$$

Similar transfer of electrons also occurs in other compounds, *e.g.*,

$$\begin{array}{llllllll} & Mg & + & S & = & [Mg^{++}] & [S]^{--} & \text{(two electrons transferred)} \\ & (2,8,2) & & (2,8,6) & & (2,8) & (2,8,8) & \\ & Ca & + & 2Cl & = & [Cl^-] & [Ca^{++}]\ [Cl^-] & \text{(two electrons transferred)} \\ \text{or} & (2,8,8,2) & & (2,8,7) & & (2,8,8), & (2,8,8),\ (2,8,8) & \end{array}$$

It is evident in such combinations, every participant atom would attain the stable inert gas configuration. Such a chemical bond with transfer of electron has been named *ionic bond* and the resultant molecules are ionic compounds.

That in a molecule formed through ionic bond the two oppositely charged ions exist and that they remain together through coulombic attraction can be easily understood from energy consideration. If r be the distance between the two sufficiently close ions, then the potential energy (U) of the pair is given by

$$U = -\frac{\epsilon^2}{r} + be^{-ar} \qquad \ldots (A)$$

where ϵ is the charge carried by an ion and (a, b) are known constants. The potential energy (U) was calculated by putting different values of r (say for $Na^+.Cl^-$ pair) eqn. (A) and these are plotted as in Fig. XXVI.1. The $U-r$ graph plotted with the experimental values from spectroscopic measurements coincides with the theoretically calculated curve especially at short interionic separations. This confirms the inherent truth in the ionic bond concept of co-existence of opposite ions in the molecule. For comparison, the potential energy of NaCl assumming non-ionic linkage (say covalent) is also plotted which gave an altogether separate curve.

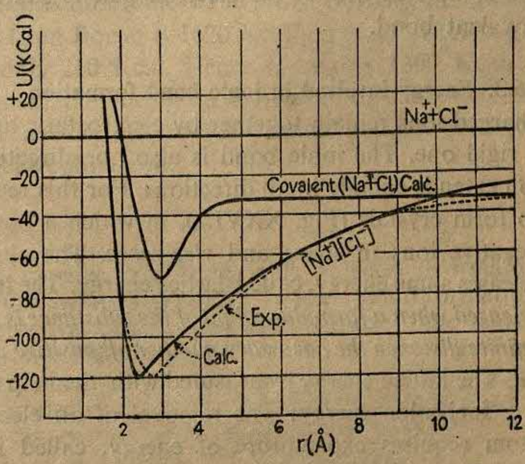
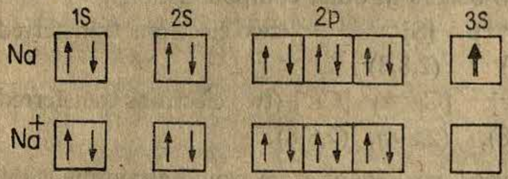
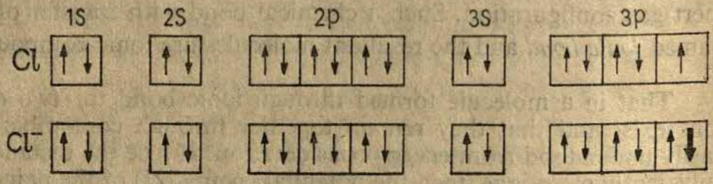


Fig. XXVI.1. Pot-energy variation with internuclear distance (NaCl)

26.2. The pairing of electrons: The wave-mechanical approach explains the bond formation more clearly. In the atoms of the inert gases, the outermost orbitals are always complete having two (paired) electrons in each orbital. The configuration is $ns^2np_x^2\ p_y^2p_z^2$. In consequence, the resultant angular orbital momentum and the resultant spin angular momentum are reduced to zero. As a result, the possibility of interaction of these paired electrons with electrons of the neighbouring atoms is minimum. In all other atoms, one or more of the outermost orbitals will be incomplete and there would be one (unpaired) electron in each of the incomplete orbitals. The theory of the chemical bonding postulates that an atom with an incomplete orbital having a single electron tends to acquire an electron of opposite spin from the incomplete orbital of a neighbouring atom and to complete its own orbital. The donor atom also, though ionised, is left with a completed orbital. For example:





The complete removal of the electron from the parent ion leads to the formation of the ionic bond. In case the electron is not completely taken away and in the completed orbital the electron pair is shared between both the atoms, it is a covalent bond.

26.3. Energy involved in ionic bond formation : In an ionic bond, two oppositely charged ions remain together by electrostatic attraction. As such the bond is not a rigid one. The ionic bond is also non-directional. The electrostatic field of an ion extends equally in all directions. For this reason such ions can cluster together to form crystals (Fig. XXVI.2), in which a positive ion would be surrounded by negative ions in space and *vice-versa*. The clustering of the ions into position releases some energy, called lattice energy. **The lattice energy** *is the amount of energy released when a formula-weight of the substance is produced by bringing together from infinite distance the necessary number of positive and negative ions forming the crystal.* The lattice energy is measured with the help of Born-Haber cycle (Sec. 9-11).

Ionisation energy: The removal of an electron or electrons from a neutral atom requires expenditure of energy, called ionisation energy. Quantitatively, *the ionisation energy is the amount of energy necessary to remove one electron from every atom of a gm-atomic weight of the element.* The ionisation energy values of some univalent elements are given in the table below.

Electron affinity: Neutral atoms may take up one or more electrons to fill up their incomplete orbitals. In this process, an amount of energy is released. *The amount of energy released when one electron is picked up by every atom of a gm-atomic weight of the element is called the electron affinity of the element.* Some electron affinity values (I_0) are tabulated below. The ionisation energy is always higher than the electron affinity. The electron affinity of metals is considered to be negligible.

TABLE : IONISATION ENERGY AND ELECTRON AFFINITY
(Kcal/gm-atom)

Element	F	Cl	Br	I	H	Li	Na	K
I_0	429	299	272	241	312	124	117.9	99.7
E_0	98.5	86.5	81.5	74.2	16.5	—	—	—

I_0 = ionisation energy ; E_0 = electron affinity

In the formation of an ionic bond, ionisation energy is to be supplied in removing the electron from one atom and energy of electron affinity is available when the electron enters the other atom. If the difference of these two energies be relatively small then the bond would be an ionic one. In NaCl, the ionisation

energy, $Na \rightarrow Na^+ + \epsilon - 118$
the electron affinity, $Cl \rightarrow Cl^- - \epsilon + 86.5$
$\therefore$ $Na + Cl \rightarrow Na^+ + Cl^- - 31.5$ Kcal.

The difference being small, it is an ionic bonding. This small energy is easily compensated by the lattice energy released during the formation of the crystals. Where the difference of I_0 and E_0 is large, the lattice energy is not sufficient to supply the deficiency in energy, the bond is non-ionic, as in BCl_3. In BCl_3, the ionisation energy in removing 3 electrons from Boron is 1620 Kcal/gm atom. Their addition to 3 gm-atoms of chlorine is only 260 Kcal. Hence $I_0 - E_0 = 1360$ Kcal. This large amount of energy is not available during the formation of the bonds. Hence in this case the bonding is such that the electrons are shared and not donated and accepted. BCl_3 is thus a covalent compound.

26.4. Variable Valency

The transitional elements usually exhibit variable valence. Normally the electrons present in the outermost orbitals take part in ionic bond formations as we have seen in NaCl. After removal of the outermost electrons, the remaining core has an inert gas structure (s^2p^6) showing stability. But in the case of transitional elements, the core (after removal of outer electrons) is not quite stable. These cores may lose one or two electrons from the outermost orbital of the *core*. For example, iron shows valences two and three in the following way:

$Fe(26) \rightarrow 1s^2 2s^2 2p^6 3s^2 3p^6 3d^6 4s^2$ *i.e.* (2,8,14,2)
$Fe^{2+} \rightarrow 1s^2 2s^2 2p^6 3s^2 3p^6 3d^6$ *i.e.* (2.8.14)
$Fe^{3+} \rightarrow 1s^2 2s^2 2p^6 3s^2 3p^6 3d^5$ *i.e.* (2,8,13)

One *d*-electron is also given up for ionic bond formation. There is another type of variable bonding. Metals of group IVA and VA have outermost electrons in *s*- and *p*-orbitals. Sometimes only part of them participate in bonding. For example: Tin has the structure.

$$\text{Sn(50)} \rightarrow 2,8,18,18,4. \quad (5s^2 5p^2)$$

(*a*) When all the 4 electrons of the outermost shell take part in bonding, it is tetravalent. In such a case the four electrons first distribute themselves into four orbitals of single electrons as $5s^1 5p^3$. Then these four electrons accept four opposite-spin electrons from other atoms to complete the orbitals, Such compounds are usually covalent.

(*b*) But sometimes $5s^2$ electrons remain undisturbed. Only the two *p*-orbital single electrons are removed to neighbouring atoms to complete the orbitals of the latter. These bi-valent tin compounds are ionic in character.

COVALENCY

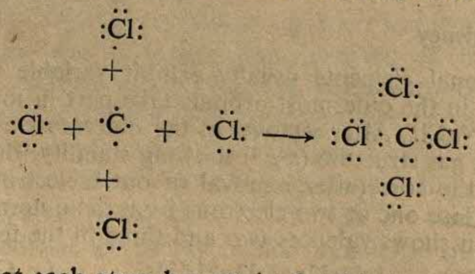
26.5. The Covalent bond

It was G. N. Lewis who pointed out first that it was possible for atoms forming a molecule to attain inert gas structure even without any transference of electron from one to the other. Lewis (1916) proposed that the union of atoms in molecules like H_2, Cl_2 etc. and in most organic molecules, resulted from *sharing of a pair of electrons* between atoms in such a way as to give complete octets for the participating atoms. For example: a chlorine atom has seven electrons in the outermost shell. When two atoms unite to form a molecule of Cl_2, each atom would contribute an electron to make a pair to be shared by both the atoms;

$$:\overset{..}{\underset{..}{\text{Cl}}}. + \cdot\overset{..}{\underset{..}{\text{Cl}}}: \; = \; :\overset{..}{\underset{..}{\text{Cl}}}:\overset{..}{\underset{..}{\text{Cl}}}:$$

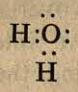
There is thus a common pair of electrons, supposed to belong to both the atoms, which counts in completing the octet round each atom. The central pair of electrons links the two atoms. This type of linking between two atoms by joint sharing of two electrons, one contributed by each participant, was named *covalency* (or *covalent bonding*) by Langmuir.

To cite other examples: Carbon has four electrons in the outermost shell and it needs four electrons to complete the octet. These four may be obtained by common sharing of electrons with four chlorine atoms, as follows:

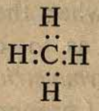


$$\begin{array}{ccccccc} & & :\overset{..}{\text{Cl}}: & & & & \\ & & + & & & & :\overset{..}{\text{Cl}}: \\ :\overset{..}{\underset{..}{\text{Cl}}}\cdot & + & \cdot\overset{\cdot}{\underset{\cdot}{\text{C}}}\cdot & + & \cdot\overset{..}{\underset{..}{\text{Cl}}}: & \longrightarrow & :\overset{..}{\underset{..}{\text{Cl}}}:\overset{..}{\underset{..}{\text{C}}}:\overset{..}{\underset{..}{\text{Cl}}}: \\ & & + & & & & :\underset{..}{\text{Cl}}: \\ & & :\overset{\cdot}{\underset{..}{\text{Cl}}}: & & & & \end{array}$$

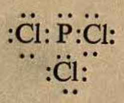
It will be noticed that each atom has attained stable inert gas configuration. In the case of hydrogen, instead of an octet, a duplet of electrons will be sufficient to produce nearest inert gas (Helium) configuration. Similarly, the formations of methane, water, phosphorus trichloride take place through covalent bonding, as:



$$\begin{array}{c}\mathrm{H:\overset{\cdot\cdot}{\underset{\cdot\cdot}{O}}:}\\ \mathrm{H}\end{array}$$

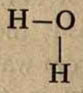


$$\begin{array}{c}\mathrm{H}\\ \mathrm{H:\overset{\cdot\cdot}{\underset{\cdot\cdot}{C}}:H}\\ \mathrm{H}\end{array}$$

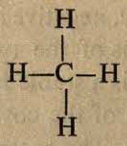


$$\begin{array}{c}\mathrm{:\overset{\cdot\cdot}{\underset{\cdot\cdot}{Cl}}:\overset{\cdot\cdot}{\underset{\cdot\cdot}{P}}:\overset{\cdot\cdot}{\underset{\cdot\cdot}{Cl}}:}\\ \mathrm{:\overset{\cdot\cdot}{\underset{\cdot\cdot}{Cl}}:}\end{array}$$

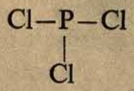
Ordinarily, the valence bond is represented by a line between atoms, as



$$\begin{array}{l}\mathrm{H{-}O}\\ \quad|\\ \quad\mathrm{H}\end{array}$$



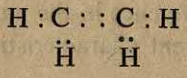
$$\begin{array}{c}\mathrm{H}\\ |\\ \mathrm{H{-}C{-}H}\\ |\\ \mathrm{H}\end{array}$$



$$\begin{array}{c}\mathrm{Cl{-}P{-}Cl}\\ |\\ \mathrm{Cl}\end{array}$$

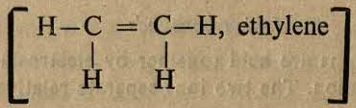
Each covalent bond is thus equivalent to a pair of electrons. In unsaturated compounds, it may be necessary for two atoms to share jointly more than one pair of electrons, as in ethylene, acetylene, etc.

$\mathrm{H:C\,\vdots\vdots\,C:H}$



$$\begin{array}{c}\mathrm{H:C::C:H}\\ \mathrm{\overset{\cdot\cdot}{H}\quad\overset{\cdot\cdot}{H}}\end{array}$$

[$\mathrm{H{-}C\equiv C{-}H}$, acetylene]



$$\left[\begin{array}{l}\mathrm{H{-}C=C{-}H}\text{, ethylene}\\ \quad\ |\qquad |\\ \quad\ \mathrm{H}\qquad\mathrm{H}\end{array}\right]$$

As with ionic bond, we may consider the energy changes in the formation of a covalent bond to find out its stability. In the case of CCl_4 formed from carbon and chlorine atoms, we may calculate as:

$$\begin{array}{lll}
 & & \textit{energy absorbed}\\
\mathrm{C}(s)\rightarrow\mathrm{C\ (atom)} & ; \triangle H = +\ 171\ \text{Kcal} & \text{(Heat of sublimation of graphite)}\\
2\mathrm{Cl_2}(g)\rightarrow 4\mathrm{Cl} & ; \triangle H = +\ 2\times 58 = 116\ \text{Kcal} & \text{(Heat of dissociation)}\\
4\mathrm{Cl}+\mathrm{C}\rightarrow\mathrm{CCl_4} & ; \triangle H = -\ 314\ \text{Kcal} & (4\times\text{bond-strength})\\
\hline
\mathrm{C}+2\mathrm{Cl_2}=\mathrm{CCl_4} & ; \triangle H = -\ 27\ \text{Kcal} &
\end{array}$$

The formation of covalent bonds in the molecule is thus naturally expected to ensure stability from its lower energy-level.

Lewis theory explains clearly the formation of the covalent bond through sharing of electrons and also most of the chemical behaviour of covalent compounds. But the theory does not provide any answer to the mechanism of the sharing of electrons leading to the stability of molecules, or for that matter, why at all sharing should occur. An answer to this question ultimately was obtained from the application of wave mechanics.

To cite an instance, let us take H_2 molecule. In this molecule the two atoms are linked together by a covalent bond, H—H. The system consists of two protons and two electrons. When two H atoms, each with an electron in 1*s* orbital, approach each other, the electron waves overlap. In the overlapping, the two waves may be in opposition leading to destructive interference, called *anti-symmetric mode* of coupling. The result is an increase in the repulsive force so that no stable H_2-molecule would be possible. On the other hand, when the electron waves overlap in such a way as to cause constructive interference, called *symmetric mode* of coupling, the electron density (proportional to ψ^2) in the region between the nuclei increases. This higher electron density, negative in character, 'cements' the two protons of the two nuclei (Fig. XXVI.3). The result is a stable H_2 molecule. This is the explanation of the covalent bonding from wave properties. The excess electron density in the vicinity of the nuclei lowers the potential energy

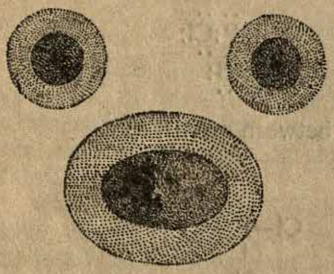


Fig. XXVI.3

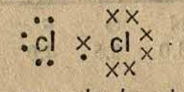
26.6. Properties of Ionic and Covalent Compounds

Owing to the difference in the nature of bonding the ionic and covalent compounds exhibit different characteristics.

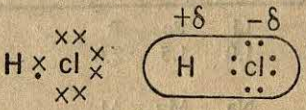
Ionic compounds	*Covalent Compounds*
1. The ions are held together by electrostatic attraction. The two ions separate relatively easily.	1. The atoms are held together by shared electrons. They cannot be separated except by chemical decomposition.
2. The ionic compounds have no spatial isomerisem.	2. They can have different spatial arrangements and exhibit isomerism.
3. They are non-rigid and the bond are non-directional.	3. Their bonds are rigid and are directional in nature.
4. In their crystals, the positive and negative ions cluster alternately producing giant molecules.	4. Crystal lattices are are built-up of molecules and not ions. The molecules are held together by weak van der Waals forces.
5. Ionic compounds are hard and have high m.pt. and b.pt. This is because more energy is required to overcome the electrostatic forces.	5. The intermolecular forces are weak and hence the crystal lattice is easily ruptured. These compounds are soft and have low melting and low boiling points.
6. Ionic compounds in molten state or in aqueous solution conduct electricity.	6. Covalent compunds are non-conductors as they do not ionise.
7. Ionic compounds are usually soluble in polar solvents like water. They are insoluble in non-polar solvents.	7. Covalent compounds are generally insoluble in polar solvents but usually soluble in non-polar solvents.

26.7. Polarity of a bond

In a covalent bond a pair of electrons is shared between two atoms. If the two atoms linked by the bond be identical (A_2-type), say H_2 or Cl_2, then the influence of the two atoms on the electron-pair is the same and the bond is said to be *non-polar*. But if the bond is formed between two different atoms (A-B type), say HCl, then the electron pair is unequally shared. Chlorine has a greater attraction for the electrons than hydrogen and it is called a *polar bond.* The electron density would be higher at the chlorine end than at the hydrogen end. The hydrogen end would be regarded as positive and the chlorine end negative. It means such a bond has a partial ionic character.



non polar bond



polar bond

The pull on the electrons would be different for different atoms and it depends upon the electronegativities of the atoms (see next section). The polarity of a bond is expressed as bond moments (see chap. VIII). The higher the bond moment, higher is the polarity of the bond. In a molecule there may occur several polar bonds. The vectorial sum of the bond moments would give the dipole moment of the molecule.

26.8. Electronegativity

It is a measure of how powerfully a bonded atom attracts the electrons in the bond. Flourine is the most electronegative and caesium is the least electronegative of elements. Pauling has enunciated a method for appreciation of electronegativities of elements. It has been suggested, the energy that the bond in A—B would have, had it been purely covalent, is the geometric mean of the covalent bond energies of the atoms of the elements. Thus, the energy of the bond in H—I is the geometric mean of the bond-energies of H—H and of I—I;

$$D_{\mathrm{H-I}} = \sqrt{D_{\mathrm{H-H}} . D_{\mathrm{I-I}}}$$

But the observed bond energy is higher than the calculated hypothetical value, due to the ionic character of the bond. For example,

$$D_{\mathrm{H-I}} = \begin{array}{cc} \text{observed} & \text{calculated} \\ 71 \text{ Kcal} & 61 \text{ Kcal} \end{array}$$

Hence, the difference $\Delta = 10$ Kcal $= 0.4$ e.v. energy is a measure of the ionic properties shown by the bond, due to difference in the electronegativities of the bonded atoms. Δ is thus a measure of the difference of the electronegativities of A and B. If x_A and x_B denote the electronegativities of A and B, then

$$x_B - x_A = \sqrt{\Delta}$$

This relation gives only a difference of electronegativities. In order to obtain the individual electronegativity, a standard value has been set for hydrogen, such that $x_{\mathrm{H}} = 2.2$. The electronegativity of iodine is then $x_I = 2.2 + 0.4 = 2.6$. Following this principle, Pauling ascertained the electronegativities of other elements as in the Table below.

THE ELECTRONEGATIVITY SCALE (H = 2.2)

Li	Be	B		C	N	O	F
1.0	1.5	2.0		2.5	3.0	3.5	4.0
Na	Mg	Al		Si	P	S	Cl
0.9	1.2	1.5		1.8	2.1	2.5	3.1
K	Ca	Sc	Ti–Ga	Ge	As	Se	Br
0.8	1.0	1.3	1.7–1.9	1.8	2.1	2.4	3.0
Rb	Sr	Y	Zr–In	Sn	Sb	Te	I
0.8	1.0	1.2	1.9–2.2	1.9	2.0	2.1	2.6
Cs	Ba	La–Lu	Hf–Tl	Pb	Bi	Po	At
0.7	0.9	1.1	1.9–2.3	2.3	2.0	2.0	2.2
	Ra		Th				
	0.9		1.3				

A direct method for calculating electronegativity x has been proposed by Mulliken, such that, $x = (I + A)/5.6$, where I and A are the ionisation potential and the electron affinity of the atom. Though arbitrary in nature, there is a concordance in the values obtained by Paulings' and by Mulliken's methods. For example: $x_{\text{cl (Pauling)}} = 3.1$ and $x_{\text{cl (Mulliken)}} = 3.0$.

The importance of these quantities lies in the fact that they at least qualitatively reflect the chemical behaviour of the elements. The greater the horizontal separation between two atoms in the electronegativity scale (see Table above) the greater is the ionic character of a bond between them. When the separation on the scale is 1.9, the bond is 50% ionic in character.

The bond between two highly electronegative atoms is covalent as in NO or CCl_4. The bond linking two elements of low electronegativity is a metallic one as in Brass (Cu + Zn). The bond type between a highly electronegative and a low electronegative element is ionic as in KCl. Also, the greater the separation of two elements in the electronegativity scale, the stronger will be the bond between them.

From the electronegativity scale, an empirical assessment of the ionic character of the bond can be made (Pauling).

$x_B - x_A$	0.0	0.4	0.8	1.0	1.2	1.6	2.0	2.4	2.6
Ionic character (%)	0	3	12	18	25	40	54	68	74

26.9. Fajan's Rules

In the electrovalent linking the positive and the negative ion approach one another closely. If the cationic charge be high (especially when its volume is small) then it exerts a strong pull on the electron cloud of the anion. This causes distortion of both the ions. The electron density between the two ions increases. In fact there is some sharing of the electrons between the ions. In other words, the bond becomes partly covalent. In case of very large distortion, the bond would be transformed into a polar covalent bond (Fig. XXVI.4).

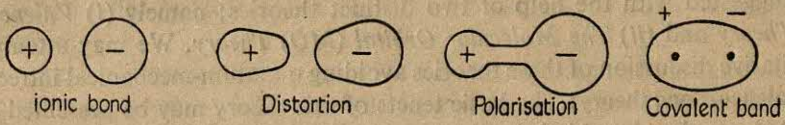


Fig. XXVI.4

The distortion would be less if the anionic volume be small and the cationic volume large. *Fajan's Rules* indicate the conditions favouring electrovalency and covalency.

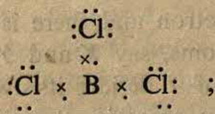
(*a*) Electrovalency is favoured with (*i*) low positive charge (*ii*) small anion and (*iii*) large cation.

(*b*) Covalency is favoured with (*i*) high positive charge (*ii*) large anion and (*iii*) small cation,

26.10. Deviation from the Octet Rule

There are instances where the octet rule governing bonding of atoms is not obeyed. There are two types of deviations.

(*i*) *Incomplete Octet:* The compounds like $BeCl_2$ and BCl_3 are covalent compounds. But there are not sufficient electrons available to fill up the octet. As such the valency shall remain with less than eight electrons, e.g.,



$$\begin{array}{c} :\ddot{\mathrm{Cl}}: \\ \times\cdot \\ :\ddot{\mathrm{Cl}} \times \mathrm{B} \times \ddot{\mathrm{Cl}}: \end{array}$$

; (Boron atom has an incomplete octet)

(*ii*) *Enlarged octet.* There are stable covalent compounds like PCl_5, SF_6 etc. where more than eight electrons may occur in the valence shell. According to Sidgwick, the maximum covalency of an element of the Vth or VIth period is 6 (*i.e.* 12 electrons). On this basis, the structures of PCl_5 and SF_6 will be:

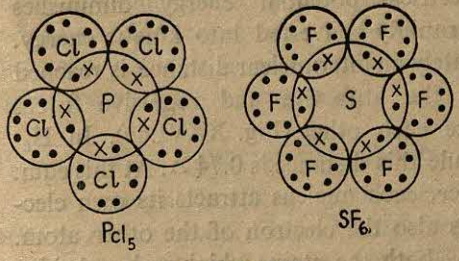


Fig. XXVI.5

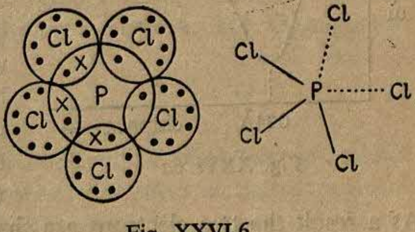


Fig. XXVI.6

But Sugden suggested that bonding in such compounds may also be effected through a single electron. Such a bond connecting two atoms by a single electron is called a **Singlet**. In PCl_5, there are three covalent bonds and two singlet bonds, See Fig. XXVI.6. The singlet bond is shown by dotted line. Now-a-days a better understanding of such compound formation is available from hybridisation,

26.11. The Covalent Bond: The Orbital Concept

The explanation for the formation a stable bond by sharing of electrons has been suggested with the help of two distinct theories; namely (*i*) *Valence-Bond* (*VB*) *Theory* and (*ii*) *The Molecular Orbital* (*MO*) *Theory*. We may attempt here a qualitative discussion of these theories avoiding quantum-mechanical intrecacies.

Valence-Bond theory: The basic tenets of this theory may be presented as:

(*i*) A covalent bond is formed when an orbital of one atom happens to overlap the orbital of the other atom to which it is going to be linked. Only the orbitals of the outermost (valence) shell participate in this overlap. By such overlapping the two atomic orbitals give rise to a localised molecular orbital (see Fig. XXVI.3).

(*ii*) The orbitals overlapping must have only one electron each. The completed orbitals containing paired electrons do not overlap. The two single electrons must have opposite spin so that these are paired on overlapping. In fact, the overlapping tendency of the orbitals arises because it would lead to a decrease in the spin-orbital momentum.

(*iii*) The bond orbital formed through overlapping of two atomic orbitals belongs to both the nuclei. The binding force of the covalent bond is due to the attraction existing between the intervening electron cloud and the two nuclei. The greater the extent of overlap, greater will be the strength of the bond.

The overlapping may occur between *s—s*, or *p—p*, *or s—p*, and other types of orbitals.

To illustrate: Let us consider the simplest case of the bond in the H_2-molecule. A H-atom has one proton (nucleus) and an *s*-electron and there is coulombic force of attraction between them. When two H-atoms, say *X* and *Y*, approach each other, the nucleus of *X* attracts the electron of *Y* besides its own electron. In the same way, there is attraction between the nucleus of *Y* and the electron of *X*. Besides, repulsive forces also exist between the two nuclei and between the two electrons. As the two atoms come closer and closer, the electrical potential energy diminishes being rapidly converted into kinetic energy. Ultimately an internuclear distance is reached where the attractive and repulsive forces balance each other (Fig. XXVI.6*a*). In H_2-molecule this distance is 0.74 Å. At this eqm. distance, each nucleus attracts its own electron as also the electron of the other atom. As a result the two electrons are shared by both the atoms which make a bridge or bond between the two.

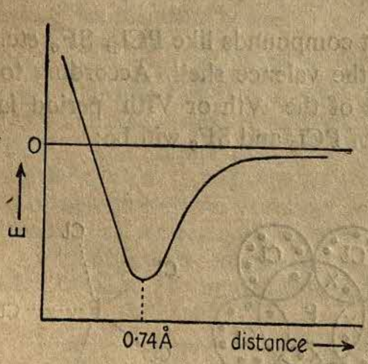


Fig. XXVI. 6*a*

The probability of finding the pair of electrons between the two atoms is high, the higher the probability the stronger is the bond. From the view point of orbitals, it is visualised that the two 1*s*-orbitals of the two atoms overlap. The two electrons of *X* and *Y* then form a common orbital governed by both the nuclei. However, such overlap would be permissible only when the spins of the two electrons are opposite. This overlap of orbitals of unpaired electrons is the essence of the VB-theory. Such cases are also found in Cl_2, HF, F_2, etc. It is not possible to have He_2 molecules because He-atom has no unpaired electron, its configuration being $1s^2$.

The spherically symmetrical *s*-orbitals do not show any preference in direction. But non-spherical *p*- or *d*-orbitals exhibit the tendency to form a bond in the direction of maximum electron density within the orbital.

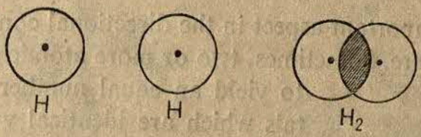


Fig. XXVI. 6*b*

In the formation of H_2O, NH_3 etc. there are *s—p* overlaps. The three *p*-orbitals in an oxygen atom are mutually at right angles. The configuration for O-atom. is $1s^2\ 2s^2\ 2p_x^2\ 2p_y^1\ 2p_z^1$. In the formation H_2O of molecule two *s*-orbitals of two H-atoms overlap the two *p*-orbitals of the O-atom. It is expected that the angle H—O—H would be 90°. But the experimentally measured angle between the two O—H bonds is 105°. The simple overlap theory hence requires some modification. This is explained from *hybridisation*, which would be discussed in the next section Similar deviation of angles occur in NH_3 and other molecules.

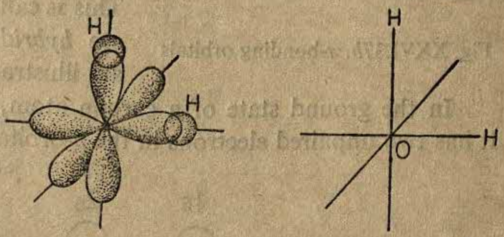


Fig. XXVI. 6*c*. Directed bonds in H_2O molecule

The valence-Bond concept also fails to explain the presence of paramagnetic properties of some molecules such as, Oxygen. According to this theory, the oxygen molecule should be $:\ddot{O} = \ddot{O}:$, two *p*-orbitals of two atoms should overlap forming σ-bonds and another two *p*-orbitals should overlap forming π-bonds. All the electrons would thus be paired leaving no unpaired electron. Yet O_2-molecule shows paramagnetic properties.

26.12. Directed Valences: Hybridisation

In the H_2-molecule, for the formation of the molecular orbital, two 1*s*-atomic orbitals are involved. The *s*-orbitals being spherical the effect is the same from whichever direction the overlapping of the orbitals might have occurred. In *s*-orbital overlapping, there is no problem of directional orientation. But directional considerations become quite important when electrons in the *p*- or *d*-orbitals take part in bond formation, as in chlorine, oxygen etc. The *p*-orbitals may overlap 'end on' as in Fig. XXVI.7*a* and give rise to a bond similar to that formed between *s*-orbitals. Such a bond is called a σ-bond. But the *p*-orbitals may also overlap 'sideways' as in Fig. XXVI.7*b*, to give rise to a bond called π-bond. A double bond consists of two bonds, one σ-bond for p_x-orbitals (say) and another π-bond from p_z orbitals.

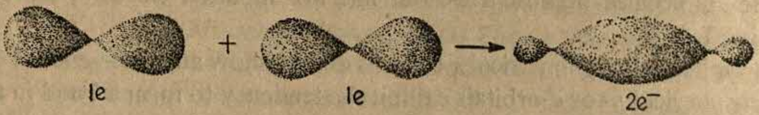


Fig. XXVI. 7*a*. T-bonding orbitals

There is another important aspect in the directional consideration of bonding which needs mention here. Sometimes, two or more atomic orbitals may combine to yield an equal number of new atomic orbitals which are identical with one another but different from the original ones. This is also justified mathematically. For example, one *s*-orbital and three *p*-orbitals of an atom may combine to give rise to four identical sp^3-atomic orbitals. This is called ***hybridisation*** and the new orbitals are ***hybrid orbitals***. We may explain this with an illustration, say the bondings in methane.

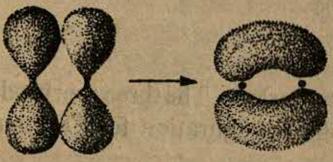
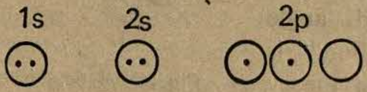
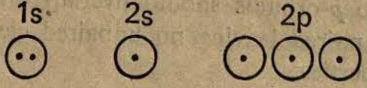


Fig. XXVI.37*b*. π-bonding orbitals

In the ground state of a carbon atom, the electronic structure is $1s^22s^22p^2$. It has two unpaired electrons in the *p*-orbitals. This can be represented as



Normally it is expected that the two unpaired electrons will form two bonds with the electrons of the combining element and carbon should exhibit a tendency to form two bonds. But four bonds do occur. It has however been found that with a small energy one of the 2*s* electrons may be excited to fill up the empty *p*-orbital, so that the structure becomes,



The carbon atom has now four unpaired electrons capable of entertaining four bonds, as in methane, combining with four *s*-electrons of four hydrogen atoms. The energy required for this initial excitation is more than compensated by the effective decrease in overall energy due to the formation of the two more extra bondings. We may next turn our attention to the orientation of these four bonds.

Of the four wave functions of carbon which would take part in bonding, one is associated with 2*s*-orbital and the other three with 2*p*-orbitals. When these will couple with 1*s*-electrons of the four hydrogen atoms, we would expect one of the bonds different from the other three. But there is undisputed chemical evidence to establish the complete identity of the four bonds in methane and the molecule possesses a high degree of symmetry. In fact, the one 2*s*-orbital and the three 2*p*-orbitals combine and hybridise to form four new *identical* sp^3-hybrid orbitals. These four hybrid orbitals are spatially oriented from the carbon nucleus towards the four corners of a regular tetrahedron. The hybrid tetrahedral orbitals are

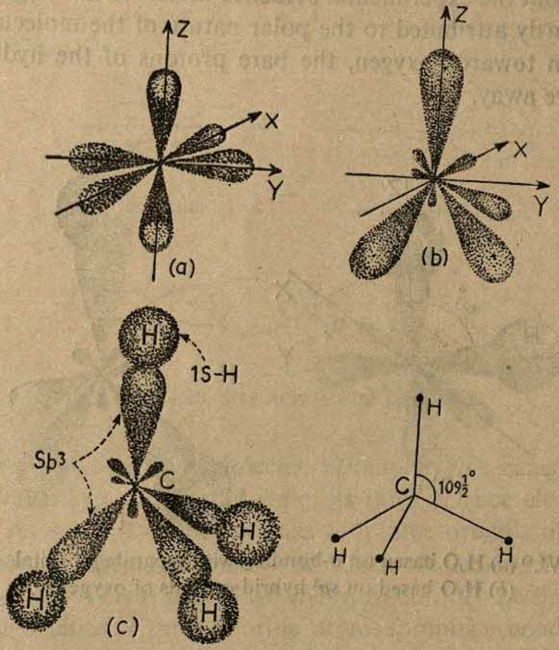
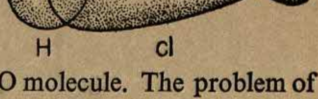


Fig. XXVI.8. (*a*) *px*, *py*, *pz* orbitals (*b*) sp^2 hybrid orbitals (*c*) sp^3 hybrids bonding with 1*s*-Hydrogen orbitals

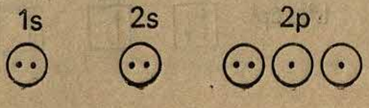
quite stable and recede as far away as possible from one another, making an angle of 109°28′. These hybrid orbitals then couple with 1*s*-orbitals of the hydrogen atoms (Fig. XXVI.8). We thus see a corroboration of the structure proposed by Le Bel and Van't Hoff.

We can now examine the structure of some very simple binary molecules to find out the part played by hybridisation. It will be seen that the shape of the molecules depends on the type of hybridisation.

(*i*) The AB-type molecules are the simplest. In such molecules, one orbital of each atom directly overlap one another. The molecules in consequence are always linear. For example, in HCl the overlap is as shown here.



(*ii*) *AB_2-type molecules.* Let us first consider H_2O molecule. The problem of directed valence also arises in the H_2O molecule. The 8-electron configuration of the oxygen atom in the ground state is



The $2p_x$-orbital is filled up and one unpaired electron is present in each of the p_y- and p_z-orbitals. The 1*s*-orbitals of two hydrogen atoms would over lap the p_y- and p_z-orbitals forming localised molecular σ-bonds. As p_y- and p_z-orbitals are at rt. angles, the two hydrogen atoms will from an angle of 90° between them [Fig. XXVI.9*a*]. But the experimental evidence indicates this angle to be 105°. The discrepancy is partly attributed to the polar nature of the molecule, for when the electron is drawn towards oxygen, the bare protons of the hydrogen repel one another and move away.

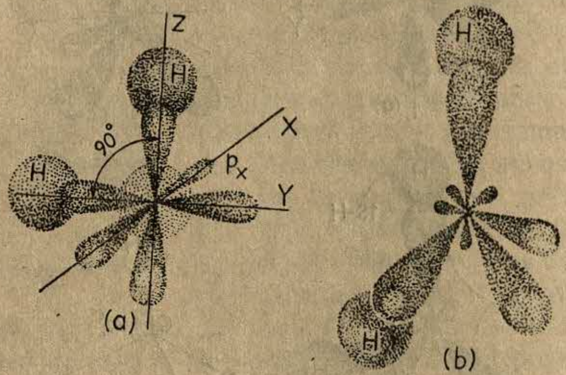
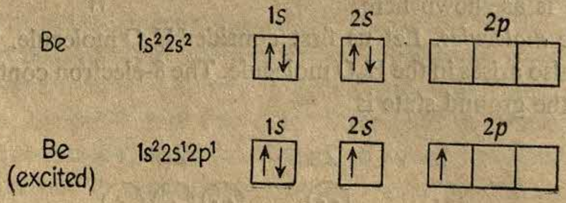


Fig. XXVI.9 (*a*) H_2O based on σ-bonding with separate *p*-orbitals of oxygen
(*b*) H_2O based on sp^3 hybrid orbitals of oxygen

An alternative viewpoint is that the 2*s*- and 2*p*-orbitals of oxygen atom undergo hybridisation to yield four equivalent sp^3-orbitals prior to bond formation. Two of these four sp^3-orbitals are occupied by pair of electrons each and do not contribute towards bonding, these are non-bonding orbitals. The remaining two sp^3-hybrid orbitals accommodate one electron apiece and their electronic charge clouds overlap with 1*s* charge clouds of two hydrogen atoms forming H_2O molecule [Fig. XXVI.9*b*]. In such a case, the angle between H-atoms would be approx. 109.5°. It is now believed that the real state is an intermediate one, for 105° angle is feasible from a mix of 1 : 4 proportion of *s*- and *p*-characters.

The water molecule is non-linear. But AB_2-molecule may also be linear as in BeF_2. In the normal state and exeited state,



That is, $2s^2$ electrons have been hybridised to an $2s^1$ and $2p^1$ electrons. It is *sp*-hybridisation. Two *p*-orbitals of two fluorine atoms now overlap these two hybrid orbitals (Fig. XXVI.10).

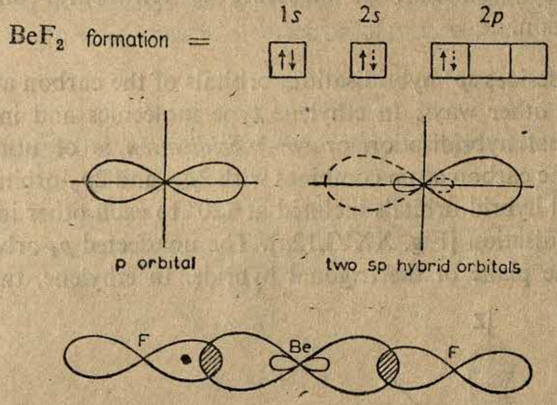


Fig. XXVI.10. Structure of BeF_2 molecule

(*iii*) *AB_3-type molecules.* BF_3 molecule belongs to this catagory.

Boron is trivalent. In the ground state, its three valence electrons are distributed as $2s^22p^1$. As such, it cannot couple with three orbitals of fluorine atoms. On excitation there is hybridisation of the three electrons into three identical orbitals as $2s^12p_x^12p_y^1$. This is indeed sp^2 hybridisation. These three orbitals then overlap with the *p*-orbitals of three fluorine atoms forming σ-bonds. The structure is planar and triangular as shown in Fig. XXVI.11. The angle F—B—F is 120°.

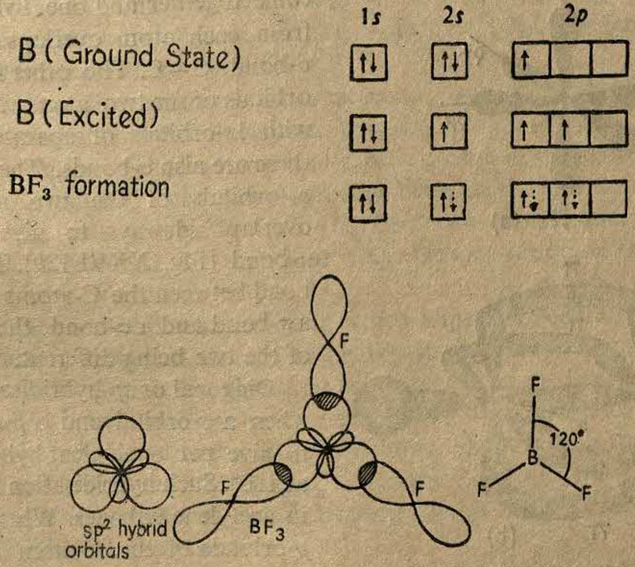


Fig. XXVI.11. The structure of BF_3 molecule

But there are AB_3-type molecules which are not planar. For example, in NH_3 molecule, the shape is pyramidal the nitrogen being present at the apex.

(*iv*) *AB_4-type molecules*: Methane CH_4 is the simplest example of this type. We have already seen that its structure is tetrahedral and is the result of sp^3-hybridisation.

26.13. π-bonds. Besides sp^3-hybridisation, orbitals of the carbon atom can undergo hybridisation in other ways. In ethylene type molecules and in aromatic molecules, the trigonal hybridisation or *sp^2-hybridisation* is of utmost importance. A $2s$-orbital of the carbon atom combines with $2p_x$- and $2p_y$-orbitals forming three identical trigonal hybrid orbitals inclined at 120° to each other in the same plane. This is sp^2-hybridisation [Fig. XXVI.12*a*]. The unaffected p_z-orbital remains perpendicular to the plane of the trigonal hybrids. In ethylene, two such C-atoms come together and one hybrid orbital from each atom overlaps to form a σ-bond, C—C. The other four hybrid orbitals of the two atoms are bonded with $1s$-orbitals of separate H-atoms; these are also σ-bonds. The remaining p_z-orbitals of the two atoms now overlap sideways to give rise to a π-bond [Fig. XXVI.12*b*]. The double bond between the C-atoms consists of a π-bond and a σ-bond, the character of the two being different.

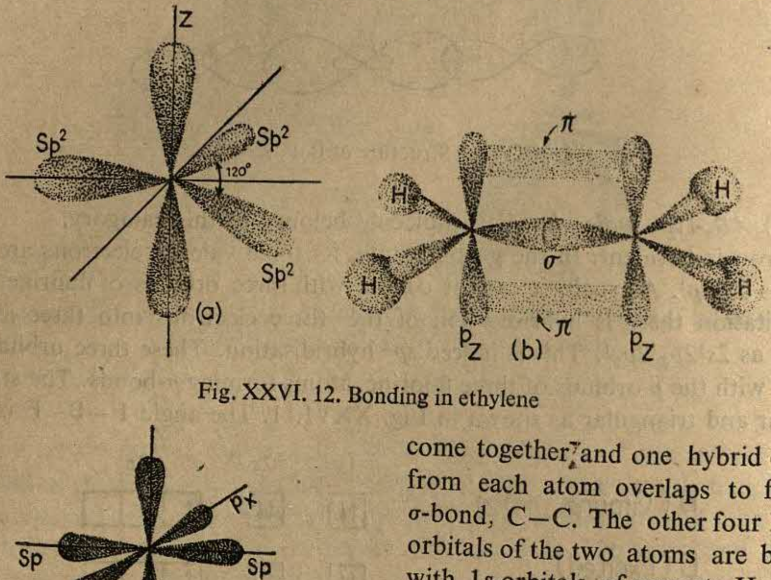


Fig. XXVI. 12. Bonding in ethylene

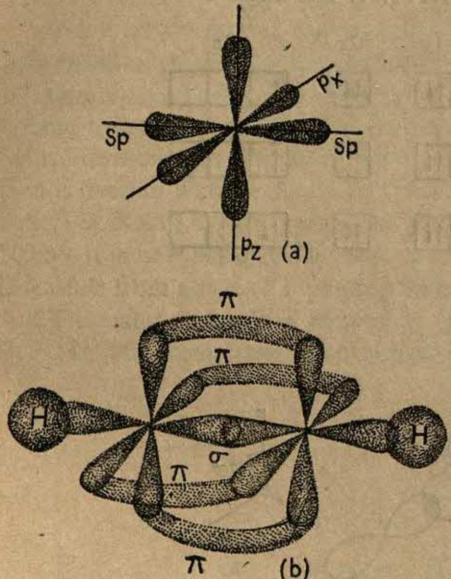


Fig. XXVI. 13. Bonding in acetylene molecule

Diagonal or *sp*-hybridisation occurs when a *s*-orbital and a *p*-orbital mix to give two equivalent hybrid orbitals at 180°. Such hybridisation is observed in acetylene linkages. When the *s*- and *p*-orbitals of the C-atom are transformed into two hybrid ones, the other two p-orbitals remain unused. When two such carbon atoms link up, one of the hybrids from each takes part to form the σ-bond between them. The other two hybrids are bounded with $1s$-orbitals of H-atoms. The p-orbitals then form a couple of π-bonds, as in Fig. XXVI.13. In fact, the two π-bonds from p_y- and p_z-orbitals combine to form a sheath of electron density between the C-atoms.

26.14. Resonance

Kekule's structure for benzene molecule may be represented as

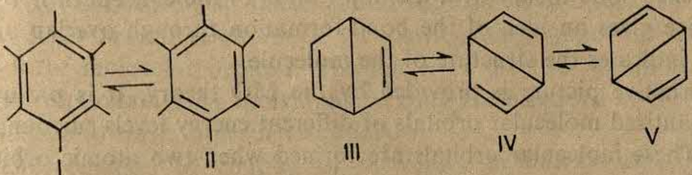


Fig. XXVI.14

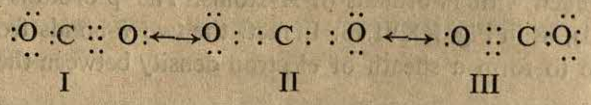
Both the bond-diagrams I and II, having alternate double bonds are equally possible. Similarly possible are the three Dewar structures.

In all these configurations, the valency requirements of the constituent atoms are satisfied. What then is the structure of benzene molecule? The true structure of the molecule is a blend of all the possible forms. It should be realised that this does not mean that some molecules have one structure and some another. The molecule will have a structure intermediate between all the possible configurations. Such a conception of multiplicity of structures is called *resonance* and the true molecule is a *resonance hybrid* of the different forms. It may be noted that resonance is not a phenomenon. since the resonating forms do not have any real existence and there is no chance whatsoever of the molecule assuming different canonical structure at different instants of time.

In different resonating forms of a molecule, only the electrons can have different arrangements but not the atoms. This is where it differs from isomerism. The number of unpaired electrons must also be the same in resonating structures. The three double bonds in benzene may occur between C-atom nos. 1—2, 3—4, 5—6 or between nos. 2—3, 4—5, 6—1. The two possibilities correspond to the Kekule structures. In the same way Dewar structures may also be represented.

The resonance hybrid is the structure which imparts maximum stability and the structure would represent the lowest energy state. Thus in benzene the heat of formation is 40 Kcal/mole less than that calculated from its bond-energy values. This difference is known as 'resonance energy'. In the resonance hybrid, the bond-lengths are also found to be less than those expected from the structures. For benzene, the C—C bond length is 1.39 Å, whereas C—C and C = C bond lengths normally are 1.54 Å and 1.35Å respectively. It suggests that every bond has a sufficient double bond character.

The resonance is not confined only to benzene or its derivatives; it is rather of frequent occurrence in various types of molecules. Even CO_2 molecule is supposed to be a hybrid one from three possible resonating structures:



$$:\overset{\cdot\cdot}{\underset{\cdot\cdot}{O}}\,:C\,\underset{\cdot\cdot}{::}\,O: \longleftrightarrow \overset{\cdot\cdot}{\underset{\cdot\cdot}{O}}:\,:C:\,:\overset{\cdot\cdot}{\underset{\cdot\cdot}{O}} \longleftrightarrow :O\,\underset{\cdot\cdot}{::}\,C\,:\overset{\cdot\cdot}{\underset{\cdot\cdot}{O}}:$$

I II III

26.15. Molecular Orbital (MO) Theory

The valence bond theory with the application of the concept of hybridisation and resonance gives an idea of the bond-formation through overlap of orbitals as well as it indicates the structure of the molecule.

An alternative picture is provided by the MO theory. It is presumed that there are quantized molecular orbitals of different energy levels surrounding both the nuclei. These molecular orbitals are formed when two atomic orbitals from two atoms combine or overlap. The atomic orbitals thereby lose their individual character. They enter into the molecular orbitals in the *aufbau* order. The molecular orbitals are designed by σ, π and δ symbols.

The number of molecular orbitals is equal to the number of atomic orbitals involved in the combination. Each molecular orbital would contain two electrons at the maximum. The electrons would occupy the lowest energy molecular orbital.

The combination of two atomic orbitals give rise to two molecular orbitals. One of these two molecular orbitals has a higher energy than the other one. The lower energy molecular orbital is known as the *bonding* *orbital* and the higher energy molecular orbital is called *anti-bonding orbital.* The antibonding orbitals are represented by putting asterisks (*) as superscripts.

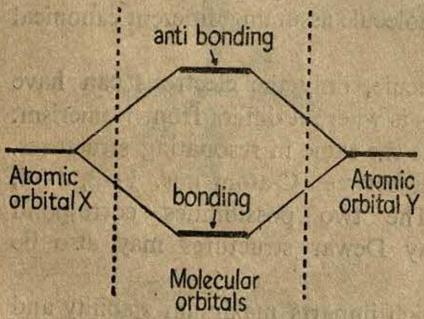


Fig. XXVI. 15. Formation of molecular orbitals from atomic orbitals

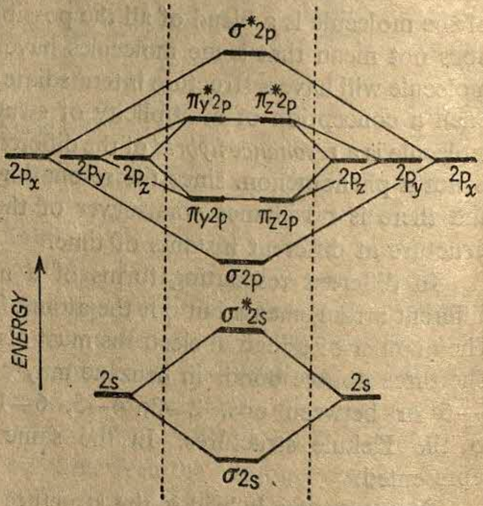


Fig. XXVI. 16. Formation of bonding and anti-bonding mol. orbitals for homonuclear diatomic molecules

The anti-bonding molecular orbital has higher energy and hence the bond is less stable, whereas the bonding orbital has lesser energy which makes the bond stable.

For homonuclear molecules such as N_2, O_2, etc.

$2s$ atomic orbital produce	$\sigma 2s$	and	$\sigma^* 2s$	molecular	orbitals
$2p_x$ atomic orbitals produce	$\sigma 2p$	and	$\sigma^* 2p$	,,	,,
$2p_y$ atomic orbitals produce	$\pi_y 2p$	and	$\pi_y^* 2p$	,,	,,
$2p_z$ atomic orbitals produce	$\pi_z 2p$	and	$\pi_z^* 2p$	,,	,,

These are diagrammatically shown in Fig. XXVI.16

In the bonding orbital there is a high electron density in between the bonded nuclei which makes the bond very stable. In the antibonding orbital the electrons scarcely exist in between the nuclei and as such the bond is unstable.

The inner orbital electrons of the participating atoms are not involved in formation of molecular orbitals. The nuclei of the two atoms with their inner shell electrons retain their individuality. Only the electrons in the outer valence shell coalesce to form molecular orbitals.

Such formation of couples of molecular orbitals is explained from the principle called *linear combination of atomic orbitals* (LCAO). The wave function associated with an orbital is denoted by ψ. Thus ψ_A, ψ_B denote the wave functions of the combining atomic orbitals and ψ_{MO} is the wave function of the molecular orbitals formed. According to LCAO principle,

$$\psi_{MO} = \psi_A + \psi_B \qquad \text{or} \qquad \psi_{MO}^* = \psi_A - \psi_B$$

$$\text{i.e.}\ \ \psi^2_{MO} = \psi^2_A + \psi^2_B + 2\psi_A \cdot \psi_B \qquad \text{and} \qquad \psi^2_{MO}{}^* = \psi^2_A + \psi^2_B - 2\psi_A \cdot \psi_B$$

$$\text{or} \qquad \psi^2_{MO} > \psi^2_A + \psi^2_B \qquad \text{and} \qquad \psi^2_{MO}{}^* < \psi^2_A + \psi^2_B$$

ψ^2-terms are measures of charge density. Obviously $\psi^2_{MO} > \psi^2_{MO}{}^*$. Hence $\psi_{MO} = \psi_A + \psi_B$ leads to a higher charge density. In this case, there is overlap of the atomic orbitals leading to increased charge density and hence greater stability of the bond. The greater the overlap, the stronger is the bond. Hence, it gives rise to bonding molecular orbital.

When $\psi_{MO}^* = \psi_A - \psi_B$, the charge density is low. The orbitals recede away. The charge density ψ_{MO}^* is less than the sum of the charge densities of the atomic orbitals: $\psi^2_{MO}{}^* < \psi^2_A + \psi^2_B$. Hence such orbitals are anti-bonding and hence less stable. A diagrammatic presentation of the electron charge densities for bonding and anti-bonding orbitals is given in Fig. XXVI.17.

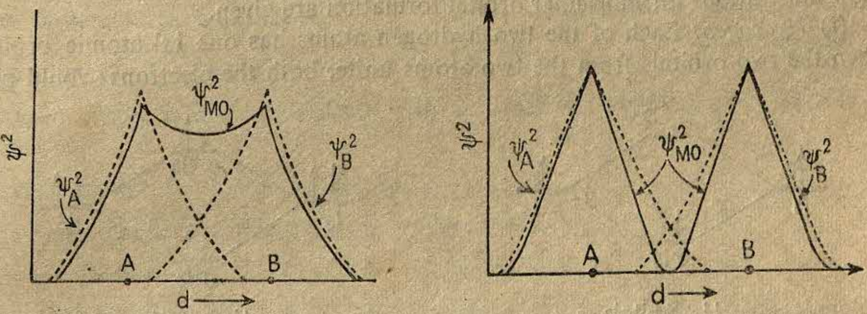


Fig. XXVI.17. Charge density distribution of (*i*) Bonding orbitals and (*ii*) anti-bonding orbitals. Dotted lines for atomic orbitals and solid lines for molecular orbitals.

The charge density distribution may be visualised from the following diagrams (Fig. XXVI.18).

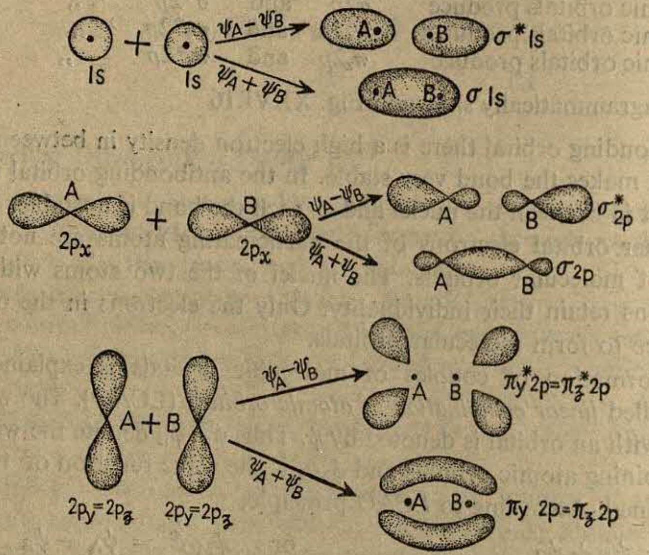


Fig. XXVI.18. Distribution of electron charge density in molecular orbitals

The energy levels for the molecular orbitals are of the following order:

$$\sigma 1s < \sigma^* 1s < \sigma 2s < \sigma^* 2s < \sigma 2p < \begin{matrix}\pi_y 2p\\ \pi_z 2p\end{matrix} < \begin{matrix}\pi^*_y 2p\\ \pi^*_z 2p\end{matrix} < \sigma^* 2p$$

The molecular orbitals are also filled up in the same order of increasing charge density with increase in number of electrons. $\pi_y 2p$ and $\pi_z 2p$ have equal levels of energy, so also $\pi^*_y 2p$ and $\pi^*_z 2p$.

The electrons present in the bonding orbitals would lead to formation of bonds and those present in the anti-bonding orbitals would oppose. The number of valence bonds (n) produced from molecular orbitals is given by $n = \frac{1}{2}(b-a)$ where

b = number of electrons in the bonding orbitals

a = number of electrons in the anti-bonding orbitals

A few illustrations for molecular orbital formation are given.

(*i*) *Hydrogen:* Each of the two hydrogen atoms has one $1s^1$ atomic orbital. When the two orbitals from the two atoms unite, both the electrons would pass

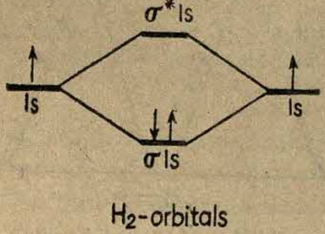


Fig. XXVI.19. H_2 orbitals

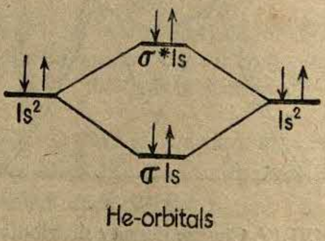


Fig. XXVI.20

into the $\sigma 1s$ orbital. σ^*1s would remain empty. Hence, the number of valence bonds $= \frac{1}{2}(2-0) = 1$.

(*ii*) *Helium*: The electronic configuration is $1s^2$. If we assume that two helium atoms would come to unite, then the four electrons would occupy the $\sigma 1s$ an σ^*1s molecular orbitals (Fig. XXVI.21). The configuration is $[(\sigma 1s)^2\,(\sigma^*1s)^2]$.

No. of valence bonds to be produced is $n = \frac{1}{2}(2-2) = 0$
That is, there would be no bonding. Helium should be monatomic.

(*iii*) *Nitrogen*: The electronic configuration of each atom of nitrogen is $1s^2 2s^2 2p_x^1 2p_y^1 2p_z^1$. When two atoms of nitrogen approach, the orbitals of the electrons of the outer shell shall only coalesce to form molecular orbitals. The inner core with $1s^2$ electrons of K-shell will remain unchanged. The molecular orbital configurations would be [K-shells] $(\sigma 2s)^2(\sigma^*2s)^2(\sigma 2p)^2(\pi_y 2p)^2\,(\pi_z 2p)^2$ as given in Fig. XXVI.21.

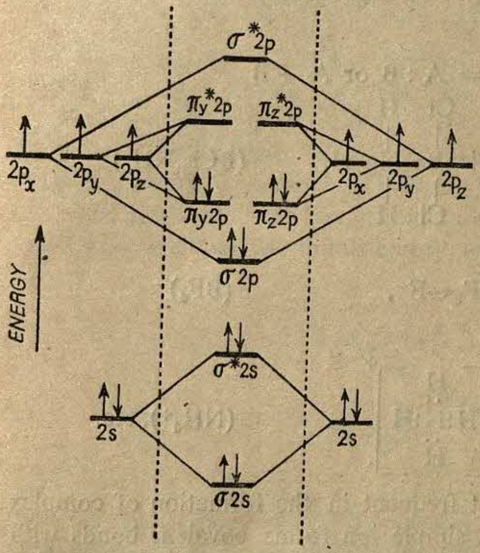


Fig. XXVI. 21
Formation of molecular orbitals in N_2

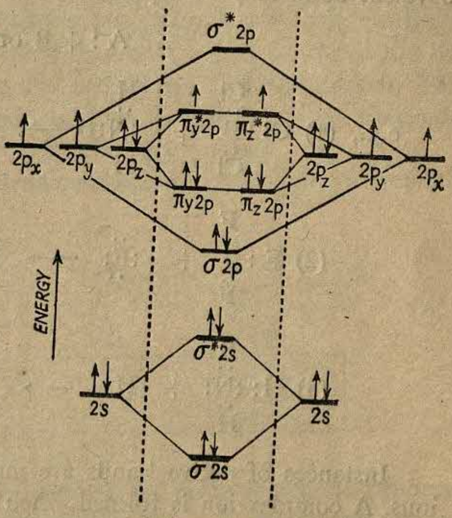


Fig. XXVI.22
Formation of molecular orbitals in O_2

The number of valences $= \frac{1}{2}(b-a) = \frac{1}{2}(8-2) = 3$.

Oxygen: There is one more electron in an atom of oxygen than those in nitrogen.

Oxygen atom: $1s^2 2s^2 2p_x^2\, 2p_y^1 2p_z^1$

The molecular orbital will have the configuration

$$\text{[K-shells]}\ (\sigma 2s)^2(\sigma^*2s)^2(\sigma 2p)^2(\pi_y 2p)^2(\pi_z 2p)^2(\pi_y{}^*2p)^1\,(\pi_z{}^*2p)^1$$

The two extra electrons will take up the positions in the next higher antibonding energy levels $(\pi_y{}^*2p)$ and $(\pi_z{}^*2p)$. This is shown in Fig. XXVI.22.

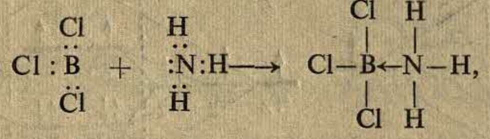
The valence number, $n = \frac{1}{2}(b-a) = \frac{1}{2}(8-4) = 2$.

Moreover in this arrangement there are two unpaired electron present in the two antibonding orbitals. The molecule will thus be paramagnetic which is an observed fact. This is a significant triumph of the MO-theory.

26.15. Dative Covalent Bond: Bonding in Complexes

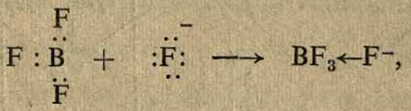
In a covalent bond between two atoms each atom contributes one electron to form the pair of electrons involved in the bond. But there are instances, where one atom provides both the electrons required. Such a bonding is called a *dative covalent bond* and is necessarily polar to a large extent. In this type of bonding the *donor* atom must possess a pair of unused electrons. Such atoms are usually found in Groups V, VI and VII of the Periodic Table. The *acceptor* must possess at least one orbital empty. Highly charged metallic ions are also found to act often as good acceptors, such as Fe^{+++}, Co^{+++} etc. Electron-rich molecules or ions such as NH_3, H_2O, CN^-, Cl^-, NO, etc. act as good donors. The formation of a dative covalent bond may be represented as

$$\mathrm{A:+B \text{ or } = A:B \text{ or } \overset{+}{A}\rightarrow\overset{-}{B}}$$

e.g., (1) 

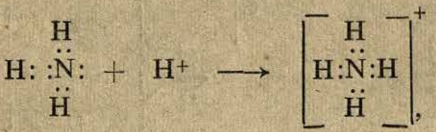
$$\mathrm{Cl:\overset{Cl}{\underset{Cl}{B}} + :\overset{H}{\underset{H}{N}}:H \longrightarrow Cl{-}\overset{Cl}{\underset{Cl}{B}}\leftarrow\overset{H}{\underset{H}{N}}{-}H,}$$

$(BCl_3.NH_3)$

(2) 

$$\mathrm{F:\overset{F}{\underset{F}{B}} + :\overset{-}{F}: \longrightarrow BF_3\leftarrow F^-,}$$

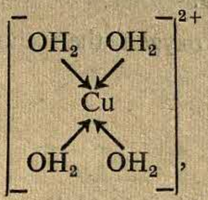
$(BF_4)^-$

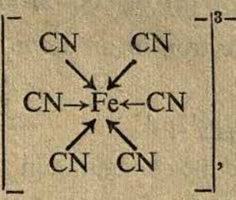
(3) 

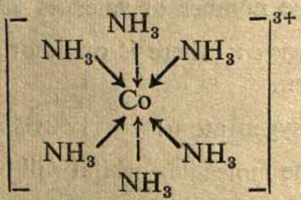
$$\mathrm{H::\overset{H}{\underset{H}{N}}: + H^+ \longrightarrow \left[H:\overset{H}{\underset{H}{N}}:H\right]^+,}$$

(NH_4^+), etc.

Instances of dative bonds are most frequent in the formation of complex ions. A complex ion is formed when a simple ion forms covalent bonds with other ions, molecules or atoms. These electron-rich ions or groups or molecules which give pair of electrons to the central metallic ion are called **ligands.** Some common instances of dative cavalency in complexes are,







$[Cu(H_2O)_4]^{++}$, $[Fe(CN)_6]^{---}$, $[Co(NH_3)_6]^{+++}$, etc.

Bonding in Coordination Complexes: Stable complexes are obtained with ions of transitional elements, for, these ions are highly charged and thus produce strong electrostatic field for attracting ligands. For the stability of the complex it is also necessary to have strong bonding between the ligands and the central ion.

If the donor ligand is highly electronegative the resulting bond will be ionic and will dissociate in aqueous solution. Ligands which have low electronegativity will form dative covalency and the complex will not easily break in solution. The stability decreases in the following order :

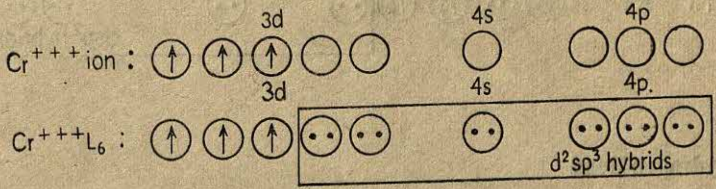
$$CN^-, NO_2^-, NH_3, H_2O, F^-, OH^-, Cl^-$$

The charge carried by the complex is the algebraic summation of the +ve charge of the central metal ion and the —ve charges donated by the ligands. The number of ligands attached to the central ion is mostly six, and in some cases it is four. Six-ligand complexes are all octahedral. Let us first examine how such complexes are formed.

In the formation of octahedral complexes, hybridisation involving *d*-orbitals always occur. Pauling has proposed that it could be possible in two ways:

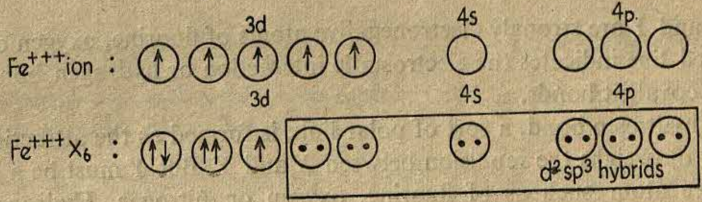
(*a*) *d^2sp^3-hybridisation:* Two vacant *d*-orbitals of a shell along with one *s*-orbital and three *p*-orbitals of the next outer shell of the central ion combine to produce six hybrid orbitals. These six hybrid orbitals overlap with suitable ligand orbitals to form σ-bonds each of which accommodates a pair of electrons. Six covalent bonds are thus formed between the central ion and the ligands. This type of hybridisation occurs with ligands of low electronegativity. Common examples are the complexes; $[Cr(H_2O)_6]^{+++}$, $[Co(NH_3)_6]^{+++}$, etc.

The bare Cr^{+++} ion has the outer electron configuration, with three 3*d*-orbitals half filled and two 3*d*-orbitals empty, as



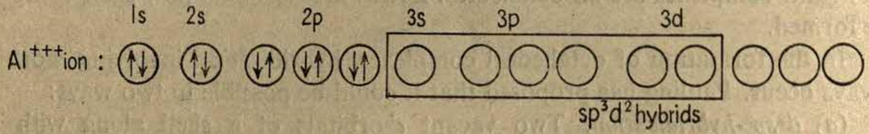
The two empty 3*d*-orbitals along with empty 4*s* and three 4*p*-orbitals produce six equivalent hybrids, occupied by six pairs of electron from the oxygen atoms of water molecules. The result is the complex, $[Cr(H_2O)_6]^{+++}$.

There are also cases where the ligands force out the unpaired electrons to make two of 3*d*-orbitals empty. The unpaired electrons thrown out couple with similar electrons in other 3*d*-orbitals, as we find, in $Fe(CN)_6$ complexes. The structure of ferric ion with five unpaired electrons is 3*d*-orbitals is

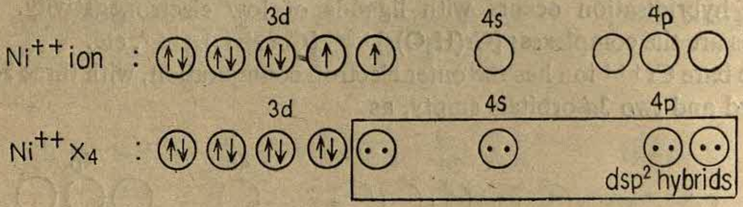


Two of the $3d$-electrons are paired off and only one unpaired electron (low spin) is left and two $3d$-orbitals become empty. Next the usual hybridisation occurs to produce six empty hybrid orbitals. The electrons from CN^- ligands fill them up carrying with them six negative charges. The result is, the complex as a whole would carry now three negative charges $[Fe(CN)_6]^{---}$.

(*b*) *sp^3d^2-hybridisation*: This type of hybridisation is favoured by ligands having high electronegativity. The unpaired electrons are left undisturbed in such complex formation and these are called 'spin free' or 'high spin' complexes. In these hybridisations, *s*, three *p* and two *d*-orbitals of the same shell are used, hence sp^3d^2. $[Al(H_2O)_6]^{+++}$ is an example of this type:



The four-ligand complexes geometrically have a planar or a tetrahedral configuration. The planar configurations result when dsp^2-hybridisation occurs as with nickel complexes.



26.15. Hydrogen Bond

A hydrogen atom when bonded with a highly electronegative atom such as flourine, oxygen, etc. acquires a positive charge. In consequence of this, such a hydrogen atom exerts an electrostatic attraction on other highly electronegative atom like fluorine, nitrogen or oxygen. There is thus a dipole-dipole or dipole-ion attraction, which has been given the name, *hydrogen bond*. This may be represented as:

$$\overset{-}{X}-\overset{+}{H}\ldots\overset{-}{Y}-A$$

where X and Y are strongly electronegative atoms of fluorine, oxygen or nitrogen. The dotted line indicates the electrostatic interaction or hydrogen bond. The full lines are covalent bonds.

The hydrogen bond, a sort of polar link, is formed as the attraction between H and Y outweighs the repulsion between X and Y. But Y must be a small electronegative atom such as of fluorine, oxygen or nitrogen. Hydrogen bonding with chlorine, sulphur or carbon is rarely observed because of the large size of the atoms.

Such a bonding is significant only with hydrogen because of the minute size of the almost bare proton which enables *Y* to make a close approach to the positive charge. The bond is not a covalent one. The experimentally measured bond energy for hydrogen bond is much less than that of a covalent bond. It approximates to 6 Kcal only, about 10% of that of a covalent link.

The bond length of hydrogen bond computed from spectroscopic and diffraction measurements is found to be greater than that of a covalent bond except in $[HF_2]^-$. In a bond like—O—H. . .O—the hydrogen atom is not located at the middle of the two oxygen atoms.

The outstanding effect of hydrogen bonding is observed in molecular association. Thus hydrogen fluoride even in gaseous state is highly associated as $(HF)_n$, due to hydrogen bonding.

Liquid water shows many abnormal physical properties; such as, high boiling pt. considering its mol. wt., high latent heat of vaporisation, surface tension, etc. These abnormalities are attributed to molecular association through hydrogen bonding. The effect of hydrogen bonding is manifested also in liquid ammonia and some liquid hydroxy compounds.

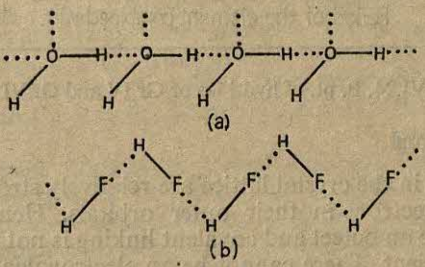
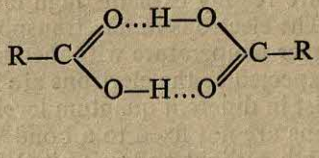
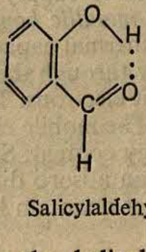


Fig. XXVI.23. Hydrogen bonds

Intermolecular and intra-molecular linking through H-bond is often observed in organic alcohols, or carboxyacids.



Dimerisation of acids



Salicylaldehyde

The hydrogen bond plays a predominant role in the helical structures of nucleic acids and other giant bio-molecules.

The effect of hydrogen-bonding is clearly demonstrated in its abnormally high boiling point. In Fig. XXVI-24 are shown the boiling points of the hydrides of Gr. IV and Gr. VI elements. With decrease in mol. wt, the b. pt. of the hydrides decreases systematically. This is observed in all the cases except in the case of water. The hydrogen bonding effect is negligible in H_2S, H_2Se, H_2Te as the electronegativities of S (2.5), Se (2.4) and Te (2.1) are close to that of hydrogen H (2.1). If there were no strong H-bond in water, it would have boiled approximately at −80°C, the point X. But it really boils at a much higher temperature of 100°C.

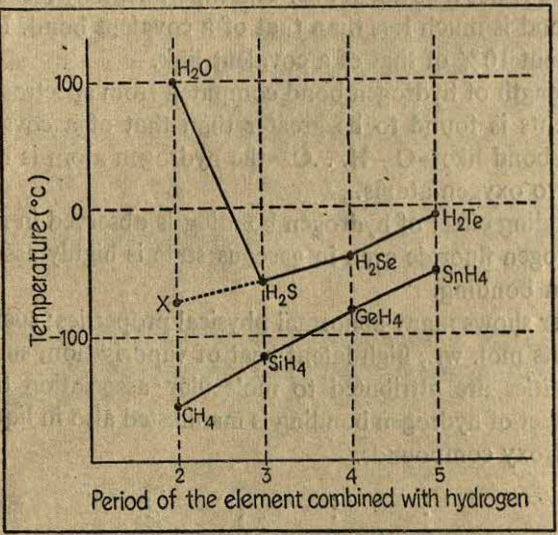


Fig. XXVI.24. B. pt. of hydrides or Gr IV and Gr VI elements

26.17. The Metallic Bond

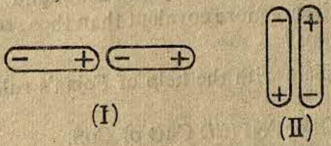
The metal atoms in the crystal lattice are relatively strongly bound. The metal atoms have 1 ∼ 3 electrons in their outer orbitals. Hence two of them cannot mutually complete an octect and covalent linking is not possible as the number of electrons is insufficient. There cannot be an electrovalent linking as transfer of electrons would not lead to octet formations. It has been postulated that the electrons in the outer shell of the metal atoms in the crystal are free and mobile. The mobile electrons move about and do not belong to any particular atom. The solid metal is visualised as a matrix of positive ions with moving electrons all around. These electrons do supply a force of cohesion between the metal atoms. This is known as the *metallic bond.* Such a picture readily explains high electrical conductivity and thermal capacity of metals. The electrons in fact transport electricity and heat easily through the metals. At higher temperature with increase in energy the metals emit electrons. This is indeed expected as the electrons are free and can easily escape. The mobile electrons can exist in different quantum levels depending upon the energy content. Since the electrons are not fixed to a bond with defined energy, they can absorb different wavelength of light and re-emit them easily by moving to lower quantum levels. This explains the lustre of metals.

26.18. Intermolecular Forces

The physical interaction between molecules may be of different types and it depends upon their nature.

(*i*) *Non-polar molecules*: Although weak, an attractive force always exists between two non-polar molecules. The electron distribution in such molecules is considered as symmetrical. But this symmetrical distribution is an average over a small period of time. A non-polar molecule is an oscillating system and at a given instant it has a small electrical moment, which varies with time and the average moment is zero. But the momentary dipole moment induces an opposite moment in the neghbouring molecule. This leads to an attractive force, called the **Dispersion force** between non-polar molecules. This is also known as **London force.** The potential energy of attraction is given as $-Ar^{-6}$, where A is a constant and r is the intermolecular separation. In very close proximity a repulsive force also comes into play due to overlap of electron clouds; its potential energy is of the order Br^{-n}, where n is usually between $9 \sim 12$; B is a constant.

(*ii*) *Dipole-Dipole interaction:* When two such molecules are in proximity, a dipole-dipole force appears. This force not only leads to mutual polarisation by electrostatic induction but also causes orientation of the molecules.



etc.

The potential energy in dipole-dipole system depends not only on the dipole moments of the molecules but also on the polarisability due to distortion and orientation.

(*iii*) *Ion-dipole interaction*: When dipolar molecules having a lone pair of electrons (such as H_2O, NH_3, etc.) approach a metal ion, there is an attractive force. The salt-hydrates are always formed due to this interaction of the metal ion of the salt and the lone pair of electrons of the water molecule. The dissolution of ionic compound is also the result of polar solvent molecules attracting the ions of the crystal lattice. When the ion-dipole attraction is very strong, the formation of complexes starts.

(*iv*) *Ion-induced dipole interaction*: A relatively high charged ion would easily distort the electron density of a non-polar molecule especially if the latter be of big size. Then an interaction takes place between the ion and the induced dipole formed from the non-polar molecule. The potential energy due to such interaction is given by $V = \alpha\,\epsilon/(2r^4)$, where α is the polorisability, ϵ the ionic charge (See also the liquid state, Sec. 5.1).

EXERCISES

1. Explain the different types of chemical bonds with examples. State the characteristics of these bonds. (*Patna B.Sc.*)

2. Write a short essay on 'Electronic theory of valency'. What type of bonds are present in (*i*) ethane, (*ii*) CO_2, (*iii*) SO_4^{--} (*iv*) $MgCl_2$? (*Jabalpur B.Sc.*)

3. Write a short account of the electronic theory of valency, pointing out clearly how the electronic representation can throw light on the properties of compounds. Give electronic configuration of (*i*) ammonia (*ii*) sulphuric acid and (*c*) hydrogen peroxide. (*Gauhati B.Sc.*).

4. (*a*) What are the main differences in electrovalent and covalent compounds?
   (*b*) Indicate the nature of bonds in the following:
   (*i*) Calcium carbide (*ii*) Potassium ferrocyanide (*iii*) ammonium chloride and (*iv*) carbon monoxide.

5. Explain clearly
   (*a*) (*i*) Co-ordinate bond (*ii*) hydrogen bond (*iii*) singlet link
   (*b*) (*i*) Electron affinity (*ii*) ionisation energy (*iii*) resonance energy

6. What is electronegativity of elements?

The electronegativities of elements A, B and C are 1.0, 2.5 and 3.0 units respectively. Predict the type of bonding in the compounds AC and BC. (*Delhi B.Sc.*)

7. An element (X) has atomic no. (14). (*i*) Write the electronic configuration of the element (*ii*) What will be its maximum valency? (*iii*) If all valencies be satisfied by hydrogen to produce XH_n. What will be the value of n? (*iv*) What will the geometry of the molecule? (*v*) Will the molecule have net dipole moment? (*Delhi B.Sc.*).

8. Explain:

(*i*) Why H_2O is a liquid when H_2S is a gas
(*ii*) H_2O is more polar than H_2S
(*iii*) HF is more polar than HI
(*iv*) m.p. of NaCl is much higher than that of $AlCl_3$
(*v*) $SnCl_4$ is a poor conductor of electricity and is a liquid
(*vi*) Oxides of alkaline earths are more covalent than those of alkali metals.
(*vii*) Why metals are lusturous?

9. State Fajan's Rules. Explain with the help of Fajan's rules which of the following pairs would be more covalent:

(*i*) $SnCl_2$ and $SnCl_4$ (*ii*) AgCl or AgI (*iii*) CuO or CuS.

10. How are the following distinguished?

(*a*) orbit and orbital (*b*) π-bond and σ-bond (c) covalency and co-ordinate valency.

11. What is hybridisation? Illustrate with examples. Show that the hybridisation is responsible for the shape of the molecules.

12. (*a*) If sp^3 hybridisation be involved in methane, water and ammonia molecules, why are the bond angles in the three cases different?

(*b*) On the basis of the concept of hybridisation, discuss the shape of the following molecules: BF_3, CCl_4 and NF_3. (*Punjab B.Sc.*).

13. (*a*) Explain and illustrate: sp, sp^2, sp^3 hybridisation.

(*b*) Give instances of d^2sp^3 and sp^3d^2 hybridisation.

14. Explain why

(*i*) the bond angle in CH_4 is 109.5°
(*ii*) the bond angle in H_2O is 105°
(*iii*) the C—C bond-length in C_6H_6 is 1.35Å
(*iv*) ethylene is a planar molecule and acetylene a linear molecule.

15. Represent the bondings in the molecules of NH_3, CH_2O, C_2H_4, HCN

(*i*) in Lewis electronic configuration.
(*ii*) in angular orbital diagrams.

16. Indicate the bondings in N_2 and C_6H_6.

17. Show how hybridisation explains the structures of $CHCl_3$, $CO(NH_3)_6^{+++}$, MnO_4^-.

18. (*a*) What do you mean by 'hydrogen bond'? How does it influence the physical properties of compounds?

(*b*) How does carbon atom having $1s^22s^22p^2$ electronic configuration at the ground state form four equivalent bonds in methane?

(*c*) Coordinate bond formation and Lewis acid-base reaction are analogous phenomena—Explain.

(Calcutta Univ. 1982)

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THE BOOK is intended for use by the undergraduate students in Physical Chemistry and it covers the syllabuses of all Indian Universities. The work is the fruit of more than forty five years of experience in teaching of a renowned and dedicated professor in undergraduate and postgraduate classes.

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The book gradually and logically builds up the solid foundation of a quantitative formulation in chemical sciences. The presentation has been made in a way which would not only improve the power of comprehension but would also help the students extrapolate knowledge to unknown situations. The areas in thermodynamics, kinetic theory, equilibria and kinetics have been exhaustively covered. Another feature is the presentation of modern ideas on the structure of atoms and molecules. In most cases, the latest experimental methods to establish a relation, such as in osmotic pressure, pH of solutions, etc. have been given. A large number of problems have been worked out and many more have been inserted for exercise.

We firmly believe that this book will be of immense benefit to the student community and that the teaching community will also find it adequate in its contents and style of presentation. Suggestions for further improvement of the book would be gratefully accepted.

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CHAPTER 14

DILUTE SOLUTIONS : COLLIGATIVE PROPERTIES

Dilute solutions of *non-volatile* solutes exhibit some characteristic properties. These solutions, having low concentration of solutes, are considered to behave ideally and obey Raoult's Law. Four properties of dilute solutions are being extensively studied; these are

(*i*) vapour pressure lowering of the solvent
(*ii*) elevation of the boiling point
(*iii*) depression of the freezing point and
(*iv*) osmotic pressure of the solution.

These properties such as the osmotic pressure or the elevation of boiling point, etc. are found to be independent of the nature of the particles in solution and depend only on the number of solute particles present in unit quantity of the solvent. Such properties which depend only on the number of particles in solution and not in any way on their nature are called **Colligative Properties.** This is the essential attribute of the four properties of dilute solutions mentioned above.

It would be convenient to consider the properties of dilute solutions of (*i*) *non-electrolytes* and (*ii*) *electrolytes* separately. We shall first develop some laws for the dilute solutions of non-electrolytes which are universally applicable. These laws have to be modified in the case of solutions of electrolytes, for electrolyte solute molecules undergo dissociation and thus cause a change in the number of dissolved particles. A colligative property will obviously be influenced by a change in the number of particles.

A. LOWENING OF VAPOUR PRESSURE OF SOLUTIONS

14.1. Raoult's Law for the relative lowering of vapour pressure

Consider a dilute solution of a non-volatile non-electrolyte solute dissolved in a liquid solvent. The parameters of the solvent are denoted by suffix 1 and those of the solute by suffix 2.

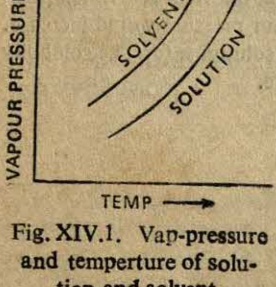

Fig. XIV.1. Vap-pressure and temperture of solution and solvent

From Raoult's Law (Sec. 13.10), we know

$$p_1 = x_1 p_1^\circ \qquad \ldots \text{(XIII.4)}$$

where p_1 and p_1° are the vapour pressures of the solution and solvent respectively. x_1 is the mol-fraction of the solvent in the solution.

Since x_1 is less than 1, hence p_1 is always less than p_1°. That is, *the presence of the solute will lower the vapour pressure of the solvent.*

It is also known that the vapour-pressure over the pure solvent or over the solution always increases with rise in temperature (Clapeyron eqn.) as in Fig. XIV.1.

Rewriting Raoult's Law, $p_1 = (1-x_2)p_1^\circ$ where x_2 is the mol-fraction of the solute.

Therefore, $\frac{p_1^\circ - p_1}{p_1^\circ} = x_2$; *i.e.* ; $\frac{\Delta p}{p_1^\circ} = x_2$ ...(XIV.1)

Raoult's Law in this form may be stated as : *In dilute solutions, the relative lowering of the vapour pressure of the solvent is equal to the mol-fraction of the solute.*

If n_2 moles of solute be present in n_1 moles of the solvent in the solution, then

$$\frac{\Delta p}{p_1^\circ} = x_2 = \frac{n_2}{n_1 + n_2} \quad \text{...(XIV.2)}$$

For a dilute solution $n_1 \gg n_2$, hence

$$\frac{\Delta p}{p_1^\circ} = \frac{n_2}{n_1} \quad \text{...(XIV.3)}$$

At a given temperature, for a definite quantity (n_1) of a given solvent, n_1 and p_1° are both constant, hence

$$\Delta p = \frac{p_1^\circ}{n_1} . n_2 = kn_2 \quad \text{...(XIV. 4)}$$

This means that *equimolar quantities of any non-volatile non-electrolyte solute dissolved in the same quantity of the same solvent would produce the same lowering of vapour pressure.* This indeed is a direct consequence of the Raoult's Law.

The lowering of vapour pressure is thus a colligative property as it depends only on the amount of the solute, *i.e.* number of molecules and not on their nature.

The validity of Raoult's law has been confirmed from innumerable experiments carried out by Raoult (1886) and subsequently by many others.

From eqm. (XIV.2), the value of $\frac{\Delta p/p_1^\circ}{x_2}$ would be unity irrespective of the nature of the solute. Raoult measured the relative lowering of vapour pressure of a number solutes in ether solution. The results:

TABLE : RAOULT'S LAW EXPERIMENTS

Solute	x_2	$\Delta p/p_1^\circ$	Ratio: $\Delta p/p_1^\circ : x_2$
Aniline	0.077	0.081	1.05
Benzoic acid	0.100	0.104	1.04
Benzaldelyde	0.130	0.132	1.02
Nitrobenzene	0.060	0.055	0.92
Methyl salicylate	0.092	0.086	0.94

These results support the law. On the other hand, when solutions of different solutes in different (suitable) solvents having the same concentration (x_2 mol-fraction) were taken, the relative lowering of vapour pressure were observed to be the same. A large number of solutions containing 1 mole of the solute in 100 moles of different solvents were prepared, *i.e.*, $x_2 = 1/101 = 0.0099 \approx 0.01$. The relative